THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE eighty-second Annual General Meeting of the Society was held at 4.30 p.m. on Wednesday, February 29th, 1956, in the Meeting Room of the Royal Society, Burlington House, London, W.1. The Chair was occupied by the President, Dr. K. A. Williams, A.Inst.P., M.Inst.Pet., F.R.I.C. The financial statement for 1955 was presented by the Honorary Treasurer and approved, and the Auditors for 1956 were appointed. The Report of the Council for the year ending February, 1956 (see pp. 252–260), was presented by the Honorary Secretary and adopted.

The Scrutineers, Messrs. P. S. Hall and R. E. Weston, reported that the following had been elected officers for the coming year—

President—K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.

Past Presidents serving on the Council—Lewis Eynon, D. W. Kent-Jones, J. R. Nicholls and George Taylor.

Vice-Presidents—D. C. Garratt, J. Haslam and H. M. N. H. Irving.

Honorary Treasurer—J. H. Hamence.

Honorary Secretary—N. L. Allport.

Honorary Assistant Secretary—R. E. Stuckey.

Other Members of Council—The Scrutineers further reported that 458 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—R. C. Chirnside, 342; A. A. Smales, 314; D. D. Moir, 283; F. C. J. Poulton, 275; S. G. Burgess, 266; A. F. Williams, 264; W. H. Stephenson, 256; W. H. C. Shaw, 192; A. L. Williams, 161.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—S. G. Burgess, R. C. Chirnside, D. D. Moir, F. C. J. Poulton, A. A. Smales and A. F. Williams.

C. H. R. Gentry, W. C. Johnson, T. McLachlan, R. F. Milton, Miss M. Olliver and S. A. Price, having been elected members of the Council in 1955, will, by the Society's Articles of Association, remain Ordinary Members of the Council for 1956.

J. R. Walmsley (Chairman of the North of England Section), F. J. Elliott (Chairman of the Scottish Section), P. J. C. Haywood (Chairman of the Western Section), J. R. Leech (Chairman of the Midlands Section), G. F. Hodsman (Chairman of the Microchemistry Group), J. E. Page (Chairman of the Physical Methods Group) and K. L. Smith (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1956.

After the business outlined above had been completed, the meeting was opened to visitors, and Sir William Slater, K.B.E., D.Sc., F.R.I.C., delivered the Bernard Dyer Memorial Lecture (see pp. 276–283). At the close of the meeting the President presented Sir William with the Bernard Dyer Memorial Medal.

ORDINARY MEETING

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 2nd, 1956, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. K. A. Williams, A.Inst.P., M.Inst.Pet., F.R.I.C.

The following paper was presented and discussed: "The Composition of Some Deposits and Muds in Estuaries, Rivers and Lakes," by J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

NEW MEMBERS

Ordinary Members

Philip Arthur Andrews, B.Sc. (Dunelm.); Lloyd Edward Radcliffe Branch, B.Sc., B.Com. (Lond.); Leonard Joseph Hamilton, B.Sc. (Lond.), F.R.I.C.; Stanley Hargreaves, B.Sc. (Lond.), A.R.I.C.; Eric Leslie Heywood, B.Sc. (Lond.); Ian Johnston, A.R.I.C.; Rowan Stanley Large; Robert Paterson McLintock, B.Sc. (Edin.), A.R.I.C.; Howard Alfred Nicholls, A.R.I.C.; Eric Barton Smith, B.Sc. (Nottingham); Francis Joseph Spillane; Ronald George Taylor, B.Sc. (Lond.), A.R.C.S.; Stanley Williams, A.R.I.C.

Junior Members

John Esam Fairbrother; Dorothy Adele Thomson, B.Sc. (Aberdeen); Ann Elizabeth Wardman.

DEATHS

We record with regret the deaths of

Philip Bilham
George Herbert Butler.

MIDLANDS SECTION

An Ordinary Meeting of the Section was held at 7 p.m. on Tuesday, March 27th, 1956, at the Gas Showrooms, Nottingham. The Chair was taken by the Chairman of the Section, Mr. J. R. Leech, J.P.

The following papers were presented and discussed: "Pharmaceutical Aspects of the Analytical Chemistry of Mercury," by G. J. W. Ferrey, B.Sc., F.R.I.C. (presented on his behalf by D. C. Garratt, B.Sc., Ph.D., F.R.I.C.); "The Microchemical Estimation of Mercury," by R. F. Milton, B.Sc., Ph.D., F.R.I.C. (presented on his behalf by W. D. Duffield).

MIDLANDS SECTION and BIOLOGICAL METHODS GROUP

A Joint Meeting of the Midlands Section and the Biological Methods Group was held at 7 p.m. on Wednesday, April 11th, 1956, at the University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Midlands Section, Mr. J. R. Leech, J.P.

The subject of the meeting was "The Fundamental Bases of Microbiological Assay" and the following papers were presented: "The Physiological and Biochemical Background of Microbiological Assay," by R. H. Nimmo-Smith, M.A., D.Phil., M.B., Ch.B. (see summary below); "The Influence of Physical Factors on the Microbiological Assay of Antibiotics," by J. W. Lightbown, M.Sc., Dip. Bact., F.P.S. (see summary below); "Practical Considerations of Microbiological Assay," by K. A. Lees, F.P.S., D.B.A. (see summary below).

The Physiological and Biochemical Background of Microbiological Assay

Dr. R. H. Nimmo-Smith said that biosynthesis of new cell material involved the intermediation of a large number of essential metabolites—components of proteins, of nucleic acids, of coenzyme systems and so on. Micro-organisms varied in their ability to synthesise their own essential metabolites. A failure to synthesise any one was reflected by a failure to grow in a defined medium unless the metabolite was present in adequate concentration. Microbiological assay exploited this situation and was based upon a relationship between growth of the test-organism and concentration of added metabolites. For the proper conduct of assays some understanding of microbial growth-cycles and modification of their pattern by limiting concentrations of a single essential metabolite was necessary.

The Influence of Physical Factors on the Microbiological Assay of Antibiotics

Mr. J. W. Lightbown said that, if the theory relating to the radial diffusion of a substance into nutrient agar was examined, deductions could be made that were helpful in designing and improving cup - plate assays of antibiotics and growth factors. A theoretical approach to this problem had been made by K. E. Cooper and D. Woodman (*J. Path. Bact.*, **1946**, **58**, 75), but the formula obtained by these workers was based on linear diffusion and was not strictly applicable to radial diffusion. In fact, K. E. Cooper

(*Nature*, 1955, **176**, 510) found a better agreement between this theory and practice when using linear diffusion than was found with radial diffusion.

A theoretical expression for radial diffusion was arrived at independently by J. Vesterdahl (*Acta Path. Microbiol. Scand.*, 1947, **24**, 273) and J. H. Humphrey and J. W. Lightbown (*J. Gen. Microbiol.*, 1952, **7**, 129). This expressed the radius of the zone of inhibition, r, to be expected when a quantity, M, of antibiotic, with a diffusion constant D, was allowed to diffuse into agar of thickness h, which was seeded with a test organism whose sensitivity to the antibiotic was σ. If the duration of the diffusion before the zone was fixed was t, then $r^2 = 9{\cdot}21\ Dt\ (\log M - \log 4\pi hDt\sigma)$. The validity of this expression had been shown experimentally by Humphrey and Lightbown, and certain deductions of importance in cup-plate assays could be made.

The first of these was that the square of the diameter of the zone of inhibition was proportional to log concentration of antibiotic in the cup. This they had found to be so for the tetracyclines, viomycin and erythromycin, when assayed with *Bacillus pumilus*, also for penicillin when assayed with either *Staphylococcus aureus* or *Sarcina lutea*. However, when penicillin or streptomycin was assayed with *Bacillus subtilis*, a linear relationship with the zone diameter was observed. The difference between the two relationships would only be obvious if the dose intervals were large or if a very accurate assay was performed.

It followed from the theory that the sharpness of the zone edge would vary directly with the diameter of the inhibition zone and inversely with the duration of diffusion before the incubation of the assay plate.

The slope of the dose-response curve was given by the expression—

$$\frac{d_1^2 - d_2^2}{\log \frac{M_1}{M_2}} = 9{\cdot}21\ Dt,$$

d_1 and d_2 being zone diameters given by concentrations M_1 and M_2, respectively. It was thus obvious that the slope was only affected by the diffusion constant of the antibiotic and the period allowed for diffusion and not by the thickness of the agar. It was independent of the sensitivity of the test organism but was affected by the rate of growth of this organism, which influenced t.

In order to increase the sensitivity of an assay one could only reduce σ or h, or increase t. Increase in t invariably produced hazy edges, and if h was reduced too much, accuracy was lost owing to increased percentage variation in the thickness of the agar due to unevenness of the assay plates. The value for σ could be decreased by choosing a more sensitive test organism and possibly by adding a sub-inhibitory concentration of the antibiotic being assayed to the assay agar.

Finally, Mr. Lightbown demonstrated how the sensitivity of the test organism to an antibiotic might vary at different depths in the agar. This happened with streptomycin, viomycin, erythromycin, neomycin and albomycin. The effect could be very marked under certain conditions and it was desirable, when assaying these antibiotics, to measure the zone diameter at the surface of the agar.

Practical Considerations of Microbiological Assay

Mr. K. A. Lees said that the term microbiological assay implied an estimation of the comparative activity of a sample and defined reference standard against a chosen test organism. Only when absolutely pure substances, in the sense that impurities present were inactive, were being assayed in terms of one another was it justifiable to employ different methods in different laboratories. Mixed preparations implied the need for rigorous standardisation of test organism and other assay variables. Liquid-tube methods were more sensitive than plate methods, but were more subject to the influence of biological variation. Plate methods depended primarily on physical considerations and, because of the presence of both standard and unknown samples in the single biological-system unit, biological variation usually affected both standard and unknown equally. Plate methods were more amenable to statistical treatment and consequent day-to-day control. Each antibiotic raised individual problems, as for example with the antibiotic fumagillin. Fumagillin was not very active against bacteria or fungi, but was active against bacterial phage. Hence both phage and phage-sensitive

bacterium were inoculated into the assay agar and the fumagillin, by diffusion, inhibited the phage and, by permitting the bacterium to grow, revealed zones of growth against the clear background of phage-inhibited bacteria.

MICROCHEMISTRY GROUP

THE fifth London Discussion Meeting of the Group was held on Wednesday, April 11th, 1956, at 6.30 p.m., in "The Feathers," Tudor Street, London, E.C.4. In the absence of the Chairman of the Group, the Chair was taken by the Honorary Secretary, Mr. D. W. Wilson, M.Sc., F.R.I.C.

Mr. H. J. Cluley, M.Sc., F.R.I.C., and Mr. C. Whalley, B.Sc., F.R.I.C., introduced the subject of "Complexones in Microchemistry," after which there was an informal discussion.

PHYSICAL METHODS GROUP

THE fifty-third Ordinary Meeting of the Group was held at 6.30 p.m., on Tuesday, April 10th, 1956, in the large chemistry lecture threatre of the Imperial College of Science and Technology, South Kensington, London, S.W.7. The Chair was taken by the Chairman of the Group, Dr. J. E. Page, F.R.I.C.

The subject of the meeting was "Plant Instrumentation" and the following papers were presented and discussed: "Progress in Plant Analytical Control Methods," by B. W. Bradford, B.Sc., Ph.D., A.R.C.S., D.I.C., F.Inst.Pet.; "The Sonic Gas Analyser," by A. E. Martin, Ph.D., D.Sc.; "Automation in the Laboratory," by D. A. Patient, B.Sc., A.Inst.P.

Annual Report of the Council: February, 1956

THE past year has seen the full operation of the Society in its widened activities following the important changes first initiated in 1953. All the scientific meetings of the Society have been well attended and valuable papers have been presented. The four Sections have each held several meetings and the three Groups many more meetings still, and as a result the activities of the Society have been country-wide. On November 29th, 1955, the Society organised a special meeting at the Beveridge Hall, University of London Senate House, at which Professor J. Heyrovský, D.Sc., Ph.D., Director of the Central Institute of Polarography, Prague, and an Honorary Member, gave a lecture entitled "The Development of Polarographic Analysis" to a large audience.

A particularly successful meeting was held at Ardeer, Ayrshire, on May 20th, 1955, when a Symposium on Gas Chromatography, arranged jointly by the Physical Methods and Microchemistry Groups with the Scottish Section, was held in the Ardeer Recreation Club. Both morning and evening meetings were well attended, and in the afternoon visitors enjoyed the generous hospitality of Imperial Chemical Industries and were conducted on a tour of the Stevenston Works and Research Laboratories, the I.C.I. providing transport and excellent meals for all.

An event deserving of special mention was the first joint meeting of the Society with the Association of Public Analysts. This was held on December 10th, 1955, in the Council Chamber of the City Hall, Cardiff, having been jointly organised by the Association and the Western Section of the Society. The meeting was honoured by a Civic Welcome given by the Deputy Lord Mayor and Deputy Lady Mayoress.

The work of the newly reconstituted Analytical Methods Committee is now well under way. The appeal to Industry for funds, which was mentioned in the last Annual Report as having been launched, proved to be an outstanding success, the total contributions for 1955 amounting to £8794, with guarantees of further sums in the next two years and also a number of deeds of covenant for seven years, totalling altogether approximately £22,500. A Trust Fund has been formed and the Society is most fortunate in having Mr. Justice Lloyd-Jacob as an independent Trustee. The Analytical Methods Committee has met regularly during the year under the chairmanship of Dr. D. C. Garratt, acting in the capacity of a policy Committee for future work and as a steering Committee to the seven working Sub-Committees. In addition, the secretariat has assumed practically all of the secretarial and editing work of the Committee on Methods of Analysis of Trade Effluents, set up jointly

by the Society and the Association of British Chemical Manufacturers; three methods have already appeared in the January issue of *The Analyst*, three more are with the printers and some twenty to thirty methods are undergoing final editing to ensure a supply for publication for some months to come. Part of the Trust Fund has been set aside for a Research Studentship, which has been awarded to Mr. T. T. A. Gorsuch, B.Sc., A.R.I.C., to undertake investigations on the determination of trace elements by radiochemical techniques. It is envisaged that Mr. Gorsuch will work at the Atomic Energy Research Establishment, Harwell, under the direction of Mr. A. A. Smales. A separate Report of the first years' work of the Analytical Methods Committee is being distributed to all contributors to the Fund; a short summary is given later in this Report.*

During the present year it is hoped that the Society's headquarters and staff will be accommodated in a suite of offices on the top floor of 15–16 Belgrave Square, London, S.W.1. This is the outcome of an arrangement whereby the Society will be tenants of the Society of Chemical Industry on most advantageous terms. In addition, it is hoped that a large room will be available for holding Council and committee meetings.

The roll of the Society now numbers 1842, an increase of 43 over the membership of a year ago.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to E. H. Miller and G. W. Monier-Williams, who have completed 50 years of membership, and to N. T. Foley and C. H. Manley, who have completed 40 years.

DEATHS—The Council regrets to have to record the deaths of the following members—

H. Ballantyne	E. W. Deag	J. McLaren
F. H. Burstall	T. F. Doyle	A. More
J. Clifford	A. Green	A. Tingle (Honorary Member)
R. L. Collett	O. Jones	T. S. Tweedie

ORDINARY MEETINGS—Six ordinary meetings of the Society were held during the year and the following papers were read and discussed—

April, 1955, in London, organised by the Physical Methods Group, on End-point Detection by Physical Methods:

"The Location of the End-point in Titrimetric Procedures." By E. Bishop, B.Sc., A.R.T.C., A.R.I.C.

"End-point Determination by High-frequency Methods." By J. P. Dowdall, B.Sc., A.R.C.S., D.I.C., A.R.I.C., D. V. Sinkinson and H. Stretch, A.R.I.C.

"Spectrophotometric Titrations." By R. A. Chalmers, B.Sc., Ph.D.

"A Short Account of the Scope and Precision of Amperometric Titration." By J. Watt, B.Sc.

May, 1955, in London:

"The Detection and Determination of Traces of Polynuclear Hydrocarbons in Industrial Effluents and Sewage. Part III. The Examination of Some Gasworks Effluents." By P. Wedgwood, M.Sc., M.Inst.Gas E., M.Inst.F., A.Inst.S.P., F.R.I.C., and R. L. Cooper, M.Sc., Ph.D., A.M.Inst.Gas E., A.R.I.C.

"The Analysis of Mixtures of Phenols by Partition Chromatography and Ultra-violet Spectrophotometry." By R. M. Pearson, A.R.I.C.

"The Determination of Traces of Benzene Hexachloride in Water and Sewage Effluents." By W. Hancock, B.Sc., and E. Q. Laws, B.Sc., F.R.I.C.

October, 1955, in London:

"The Colorimetric Determination of Phosphorus in Steel and Copper-base Alloys." By W. T. Elwell, F.R.I.C., and H. N. Wilson, F.R.I.C.

"The Determination of Small Amounts of Carbon in Steel by Low-pressure Analysis." By R. M. Cook, A.Met., B.Sc. (Eng.), and G. E. Speight, A.Met., B.Sc., F.R.I.C.

"The Determination of Small Amounts of Sulphate by Reduction to Hydrogen Sulphide, and Titration with Mercuric or Cadmium Salts with Dithizone as Indicator." By E. E. Archer, B.Sc.

* *Note by Editor*—The full text of the Report of the Analytical Methods Committee is reproduced on pp. 261–275 of this issue.

November 2nd, 1955, organised by the Biological Methods Group, on the Evaluation of Anti-fungals:

"Laboratory Evaluation of Drugs for Clinical Trial Against Dermatomycoses." By H. O. J. Collier, B.A., Ph.D., M.I.Biol., and G. K. A. Smith, A.I.M.L.T.

"Some Factors in the Planning of Fungitoxicity Experiments in the Laboratory." By R. J. W. Byrde, B.Sc., Ph.D., and G. M. Clarke, M.A., Dip.Stat.

"Cattle Ringworm: Problems in the Evaluation of Treatment." By K. C. Sellers, Ph.D., B.Sc., D.V.S.M., M.R.C.V.S.

November 30th, 1955, organised by the Physical Methods Group:

"Atomic Energy and the Analyst." By A. A. Smales, B.Sc., F.R.I.C.

January, 1956, organised by the Microchemistry Group:

"Microchemical Methods in the Art Gallery and Museum." By A. E. A. Werner, M.A., M.Sc., D.Phil., A.R.I.C.

"The Ring-oven Technique and its Application in Archaeology." By H. Weisz, Dr. techn.Dipl.-Ing.

JOINT MEETING—As mentioned above, the first Joint Meeting with the Association of Public Analysts was held in December, 1955, in Cardiff. Members of the Food Group of the Society of Chemical Industry were also invited to attend. The Chair was taken by the President of the Association of Public Analysts, Mr. T. McLachlan, D.C.M., A.C.G.F.C., F.R.I.C., and the following paper was presented and discussed:

"Sucrose Loss from Ice-cream on Storage." By H. J. Evans, B.Sc., F.R.I.C., W. Kwantes, M.A., M.B., B.Chir., Dip.Bact., D. C. Jenkins, B.Sc., M.Sc., F.R.I.C., and J. I. Phillips, F.R.I.C.

NORTH OF ENGLAND SECTION—The membership of the Section is 373. Including the Summer Meeting at Blackpool, 6 meetings have been held. The following papers were read and discussed—

"The Importance of Analysis in Industry." By J. Haslam, D.Sc., F.R.I.C.

"Some Aspects of Forensic Chemistry." By G. B. Manning, B.Sc., M.B., Ch.B., F.R.I.C.

"Margarine." By W. L. Wren, B.Sc., F.R.I.C.

"Some Modern Tools of the Analytical Chemist." By J. R. Nicholls, C.B.E., D.Sc., F.R.I.C.

"The Determination of Germanium by Analytical and Spectrographic Methods." By K. V. Aubrey, B.Sc., and G. R. Gregory.

"Applications of Newer Techniques to the Analysis of Pharmaceutical Products." By D. C. Garratt, B.Sc., Ph.D., F.R.I.C.

SCOTTISH SECTION—The membership of the Section remains unchanged at 103.

Three ordinary meetings have been held, two in Edinburgh and one in Glasgow. In addition, Symposia were held on "Gas Chromatography" at Ardeer, in conjunction with the Physical Methods and Microchemistry Groups, and on "The Use of Radioactive Materials in Biological Assay" at Edinburgh, in conjunction with the Biological Methods and Physical Methods Groups and local sections of the Royal Institute of Chemistry, the Society of Chemical Industry and the Chemical Society. The 21st year of the Section's activities culminated in the Annual General Meeting held at Glasgow on January 20th, 1956, attended by the President of the Society. The Section participated in the Ramsay Chemical Dinner organised by the Chemical Group of the Federation of Technical Societies in Glasgow.

The following papers were read and discussed—

Edinburgh, April, 1955:

"The Determination of Small Amounts of Zinc in Various Materials." By J. A. Hunter, B.Sc.

"The Determination of Calcium and Magnesium in Plant Material Using Disodium Ethylenediaminetetra-acetate." By Miss E. S. R. McCallum, B.Sc., and A. M. Smith, Ph.D.

"The Chromatographic Separation and Determination of Alkaline-earth and Alkali Metals." By J. B. Headridge, B.Sc., and R. J. Magee, M.Sc., Ph.D.

Ardeer, May, 1955. Symposium on Gas Chromatography:

"Gas - Liquid Chromatography." By A. J. P. Martin, Ph.D., F.R.S.

"The Vapour-phase Chromatographic Analysis of Hydrocarbon Mixtures." By D. E. Chalkley, B.A., B.Sc.

"Techniques Used in a Study of the Boron and Silicon Hydrides." By A. B. Littlewood, B.A.

"Adsorption and Partition Methods." By C. S. G. Phillips, M.A.

"A Rapid Chromatographic Method for the Determination of Bromine-inert Impurities in Ethylene." By N. H. Ray, B.Sc., A.R.I.C.

Discussion on Katharometers as Recorders in Gas Chromatography. Opened by Dr. Keulemans and A. F. Williams, B.Sc., F.R.I.C.

Edinburgh, July, 1955. Symposium on the Use of Radioactive Materials in Biological Assay:

"The Determination of Radioactive Isotopes in Biological Samples." By R. F. Glascock, B.Sc., Ph.D.

"The Principles of Isotope-dilution Assays with Special Reference to Vitamin B_{12}." By E. Lester Smith, D.Sc., F.R.I.C.

"Bio-assay of Radio-iodinated Plasma Proteins for Clinical Use." By A. S. McFarlane, M.A., B.Sc., M.B., Ch.B.

"Isotope-dilution Assay of Antibiotics in Fermentation Liquors with Particular Reference to Benzylpenicillin and Griseofulvin." By G. C. Ashton, B.Sc.

"The Assay of Aldosterone and Other Adrenal Steroids by the $^{24}Na/^{42}K$ Method." By R. N. Jones, B.A., Sylvia A. Simpson, B.Sc., and J. F. Tait, B.Sc., Ph.D.

"Assay of T.S.H. Based on the Rate of Discharge of Radioactive Iodine from the Thyroids of Chicks." By T. Kinnear, M.B.E., M.B., M.R.C.P., M.R.C.P.E.

"Labelled Metabolic Pools for Studying Quantitatively the Biochemistry of Toxic Action." By F. P. W. Winteringham, F.R.I.C.

"The Use of ^{131}I-labelled Serum Albumin in Determining the Inter-cellular Plasma in Centrifuged Red Cells." By F. W. Jennings, B.Sc., M.Agr., I. M. Lauder, M.R.C.V.S., and W. Mulligan, M.Sc., Ph.D.

"The Measurement of Health Hazards." By J. F. Loutit, D.M., M.R.C.P.

Glasgow, September, 1955, on the Determination of Traces of Lead:

Introductory Talk. By N. L. Allport, F.R.I.C.

"Lead in Biological Materials." By S. L. Tompsett, B.Sc., Ph.D., D.Sc., F.R.I.C.

"The Determination of Lead by Square-wave Polarography." By D. J. Ferrett, M.A., D.Phil.

Grangemouth, November, 1955:

"Some Industrial Applications of Ion-exchange Materials." By T. R. E. Kressman, Ph.D., D.I.C., A.R.I.C.

Edinburgh, December, 1955:

"Statistics for Chemists (Statistical Control in Chemical Analysis)." By B. Woolf, M.A., Ph.D., F.R.S.E.

WESTERN SECTION—The membership of the Section is 88.

Attendances at meetings have been satisfactory, having regard to the scattered area of the Section. As would be expected, the joint meetings with other Societies attract the largest attendances, and this enables some propaganda work to be done on the attractions of joining the Society. The following papers were presented and discussed—

Bristol, January, 1955:

"Recent Advances in Bacteriological Examination of Water Supplies." By E. Windle Taylor, M.A., M.D., D.P.H., M.R.C.S., L.R.C.P., Barrister-at-Law.

Cardiff, February, 1955:

"Some Applications of Modern Techniques in Analytical Chemistry." By J. R. Nicholls, C.B.E., D.Sc., F.R.I.C.

Gloucester, May, 1955:

"The Role of Iodine in Analytical Chemistry." By Dr. K. Morgan.

Bristol, October, 1955, held jointly with the Physical Methods Group, on X-ray Analysis:

"The X-ray Analysis of the Structure of Vitamin B_{12}." By Dorothy Crowfoot Hodgkin, B.Sc., M.A., Ph.D., F.R.S.

"X-ray Fluorescent Quantitative Analysis as a Tool in Archaeology." By E. T. Hall, M.A., D.Phil.

"X-ray Diffraction Techniques in the Investigation of Crime." By E. B. Parkes, M.Sc., F.R.I.C.

Bristol, January, 1956:

"Industrial Application of Sequestering Agents." By R. L. Smith, B.Sc., Ph.D., A.R.I.C., and P. Womersley.

MIDLANDS SECTION—The membership of the Section is 282.

Meetings have been held in Birmingham and Nottingham. A special joint meeting with the Birmingham and Midlands Section of the Royal Institute of Chemistry was held on November 23rd, 1955, at which Professor J. Heyrovský, D.Sc., Ph.D., gave a lecture on "Modern Trends of Polarographic Analysis."

The following papers were read and discussed—

"The Analytical Chemistry of Textiles." By A. G. Hamlin, B.Sc., F.R.I.C.

"The Analytical Chemistry of Niobium and Tantalum, with Particular Reference to Steel and Allied Materials." By B. Bagshawe, A.Met.

"4-Amino-4′-chlorodiphenyl as a Reagent for the Determination of Sulphate." By A. J. Nutten, B.Sc., Ph.D., F.R.I.C.

"The Determination of Sulphur in Coals after Combustion in the Calorimetric Bomb." By H. C. Wilkinson, M.Sc., A.M.Inst.F., A.R.I.C.

"A Semi-micro Method for the Determination of Sulphur in Rubber." By B. B. Bauminger, Ph.D., A.R.I.C.

"The Determination of Sub-micro Quantities of Sulphate." By A. S. Jones, B.Sc., Ph.D., and D. S. Letham, M.Sc.

"The Use of the Mass Spectrometer in Analysis." By J. C. Robb, B.Sc., Ph.D., A.R.I.C.

"Microwave Spectroscopy." By J. Sheridan, M.A., D.Phil.

"The Analysts' Dilemma: Colour or Stability." By R. J. P. Williams, M.A., D.Phil., A.R.I.C.

"Ring-oven Technique." By H. Weisz, Dr.techn.Dipl.-Ing.

Discussion on "Spectrophotometric Titrations" opened by R. A. Chalmers, B.Sc., Ph.D., and S. J. Clark, B.Sc., Ph.D., A.R.I.C.

"Some Physical Methods for the Analysis of Phosphorus Compounds." By Dr. D. E. C. Corbridge.

"Recent Advances in Inorganic Analysis." By R. Belcher, Ph.D., F.Inst.F., F.R.I.C.

"Gas Chromatography." By J. C. Tatlow, Ph.D., D.Sc., A.R.I.C.

"Ionophoresis." By A. B. Foster, B.Sc., Ph.D.

"Ultra-micro Methods for the Analysis of Organic Compounds." By T. S. West, B.Sc., Ph.D., A.R.I.C.

MICROCHEMISTRY GROUP—Eighty-seven members have joined the Group during the year and the membership is now 529. Three meetings were held during the year, in Ardeer, Southampton and London.

London: The Annual General Meeting was held in London in January, 1956, and was followed by a meeting of the Society organised by the Group, as reported above.

Ardeer: Symposium on "Gas Chromatography" jointly with the Scottish Section and the Physical Methods Group. The papers presented at this meeting are detailed in the report on the activities of the Scottish Section.

Southampton: A joint meeting with the Mid-Southern Counties Section of the Royal

Institute of Chemistry on "Trace Elements in Archaeology and Agriculture." The following papers were read and discussed—

"Trace Elements in Archaeology." By C. F. M. Fryd, B.Sc., A.R.C.S.

"Methods for Determining the Trace-element Status of Plants." By E. J. Hewitt, B.Sc., Ph.D., A.K.C.

"The Estimation of Trace Elements in Plant Material and Soils by Means of *Aspergillus niger*." By D. J. D. Nicholas, B.Sc., Ph.D., A.K.C., F.R.I.C.

In addition to the above, the activities of the Group have been augmented by the holding of three informal discussion meetings in London. The following topics were introduced by experts and discussed by the members present—

"The Direct Determination of Oxygen in Organic Substances."

"The Micro-determination of Molecular Weight."

"The Determination of Carbon and Hydrogen."

Arising from the first meeting, a collaborative investigation into the methods of oxygen determination was initiated. This is continuing under the control of the Analytical Methods Committee.

PHYSICAL METHODS GROUP—The membership of the Group is now 572, an increase of 84 since last year.

Two Group meetings were held in London and one at Ardeer jointly with the Scottish Section and the Microchemistry Group. Another meeting was held jointly with the Western Section in Bristol. The Group also participated in the Edinburgh meeting held jointly with the Scottish Section, the Biological Methods Group and the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry and the Chemical Society.

After the Annual General Meeting on November 30th, 1954, a discussion took place on "Possibilities in the Establishment of Standard Samples for the Determination of Some Trace Elements." The following papers were read and discussed at other ordinary meetings of the Group—

Solvent Extraction—London, January, 1955:

"Solvent Extraction. Introductory Survey." By H. M. N. H. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M.

"Laboratory Apparatus for Solvent Extraction." By I. Wells, B.Sc., D.I.C., A.M.I.Chem.E.

"Fractionation of Crude Fumagillin by Distribution Methods." By R. R. Goodall, B.Sc., Ph.D., and J. K. Landquist, B.Sc., Ph.D.

"Solvent Extraction in the Analysis of Precious Metals." By W. A. E. McBryde, M.A., Ph.D.

Gas Chromatography—Ardeer, May, 1955, and Radioactive Materials—Edinburgh, July, 1955:

Details of the papers read at these meetings are given under the Scottish Section report.

X-ray Analysis—Bristol, October, 1955:

Details of the papers read at this meeting are given under the Western Section report.

Mr. R. A. C. Isbell, for six years the Honorary Secretary of the Group, retired at the Annual General Meeting and is succeeded by Mr. L. Brealey.

BIOLOGICAL METHODS GROUP—During the year the membership of the Group increased by 19 and now stands at 268.

The Summer Meeting of the Group took the form of a joint meeting with the Scottish Section and the Physical Methods Group on "The Use of Radioactive Materials in Biological Assay." The meeting was held in the University of Edinburgh on July 11th and 12th, 1955, and was supported by the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry and the Chemical Society. The papers presented at this meeting are detailed in the report on the activities of the Scottish Section.

On December 10th, 1954, an ordinary meeting of the Group was held, immediately after the Annual General Meeting for the year 1953–54. The following papers were read—

"The Evaluation of Vegetable Purgatives." By J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S., A.R.I C.

"The Disc - Plate Method of Assay with *Neurospora* Mutants for Thiamine, Pyridoxin, Choline, Inositol and *p*-Aminobenzoic Acid." By E. C. Barton-Wright, D.Sc., F.R.I.C., and N. J. Butler.

"Observations on the Biological Estimation of Vitamin E." By T. Moore, D.Sc., Ph.D.

A symposium meeting on "Biological and Microbiological Methods of Estimating Vitamin B_{12}" was held on May 13th, 1955. Five papers were read to a large audience—

Introductory Address. By F. A. Robinson, M.A., LL.B., F.R.I.C.

"The Microbiological Estimation of Vitamin B_{12} in Serum." By R. H. Girdwood, M.D., Ph.D., F.R.C.P.E., M.R.C.P.

"The Estimation of Vitamin B_{12} in Animal Feeding Stuffs with *Lactobacillus leichmannii* and *Ochromonas malhamensis* as Test Organisms." By D. H. Shrimpton, B.A., Ph.D.

"The Estimation of Vitamin B_{12} in Milk." By Margaret E. Gregory, Ph.D., A.R.I.C.

"Biological Methods of Estimating Vitamin B_{12}." By Marie E. Coates, Ph.D., F.P.S.

"A Critical Analysis of the Method of Vitamin-B_{12} Assay with *Euglena gracilis* as Test Organism." By W. R. Pitney, M.D., M.R.A.C.P.

ANALYTICAL METHODS COMMITTEE—As has already been recorded, the past year has shown considerable activity in spite of difficulties experienced during the first few months owing to inadequate office accommodation. The amount of work increased rapidly, particularly in connection with the methods of analysis of Trade Effluents; the secretariat moved to a larger office at 20 Eastcheap, London, E.C.3, at the end of August and the staff was increased to three, including a part-time graduate assistant.

The activities of the A.B.C.M. - S.A.C. Committee on Analysis of Trade Effluents has already been mentioned in some detail.

The report of the Vitamin-B_{12} Panel of the original Vitamin Sub-Committee (now disbanded) has now been completed. The Vitamin-E Panel is preparing a report on the chromatographic assay of α-tocopherol and the experimental work on the differential analysis of total tocopherols is proceeding.

The Essential Oil Sub-Committee report on the Determination of Linalol has been completed. The work of this Sub-Committee is under review and a programme is being prepared.

A report by the Pesticides Residues in Foodstuffs Sub-Committee on the Determination of Small Amounts of Total Organic Chlorine in Solvent Extracts of Vegetable Material has been completed. The future work of the Sub-Committee is at present under consideration with a view to broadening its scope

The Metallic Impurities in Organic Matter Sub-Committee, under the Chairmanship of Mr. T. McLachlan, suceeds the old Metallic Impurities in Foodstuffs Sub-Committee, the scope of its work having been broadened. Collaborative investigation is in progress on the molybdenum-blue method for arsenic. The tentative method for lead, published in 1954, is under review.

The Meat Products Sub-Committee, under the Chairmanship of Dr. H. G. Rees, succeeds the old Meat Extracts Sub-Committee, the scope of its work having been broadened. An investigation into nitrogen factors for all types of meat is in progress and methods for the determination of starch are being considered.

Following a proposal by the Microchemistry Group for collaborative work on the Unterzaucher micro method for the direct determination of oxygen, a Sub-Committee has been formed under the Chairmanship of Mr. D. W. Wilson. The results of the first collaborative experiment are now being collated.

The work of the old Standard Methods Sub-Committee, which was responsible for the preparation of the Bibliography of Standard Methods, has now been assumed by the A.M.C.; the first objective is the publication in a single volume of the methods recommended by the A.M.C. in their Reports since 1927. The methods on soap analysis and assay of scheduled poisons have now been edited according to an agreed format and two more groups—metallic impurities in foodstuffs, and vitamins—are in preparation.

A Joint Committee with the Pharmaceutical Society is to be set up under the Chairmanship of Dr. K. R. Capper to collect and publish methods of analysis of those drugs that are no longer official but are still in demand in industry.

LIAISON COMMITTEE—During the year the following appointments have been made—

B.S.I. Committees:

Mr. D. W. Wilson, Laboratory Furniture and Fittings.
Mr. M. A. Fill, Microchemical Apparatus and Laboratory Ovens,
Mr. G. Middleton, Pyridine.

Joint Library Committee, Chemical Society:

Dr. J. G. A. Griffiths was again appointed the Society's representative.

British Iron and Steel Research Association:

Dr. J. Haslam represented the Society at the Ninth Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).

Parliamentary and Scientific Committee:

Mr. G. Taylor continued to represent the Society.

The Council of the Society thanks all its representatives for the work they have carried out in the various Committees and at the various meetings during the year on behalf of the Society.

HONORARY TREASURER'S REPORT—Once again finance has given the Council much food for thought during the past year.

In the first instance the Council decided to change the financial year, which, since the inception of the Society, has ended on December 31st. With the Society's Annual General Meeting being held very early in March, this has left little time for the accounts to be audited and a balance sheet printed in time for the Annual General Meeting. With this in mind the Council decided, on the advice of the Finance Committee, that in future the financial year should end on October 31st. This new arrangement came into operation last year, so that the balance sheet for this year shows the accounts for 10 months only, but in all subsequent years the balance sheet will cover a full 12 months.

For some years now the Society has relied on a grant from the Chemical Council to balance its publications accounts. Early in the year the question of increasing the price of *The Analyst* and *Analytical Abstracts* to outside subscribers and of increasing the subscription to the Society was considered at a Joint Meeting of the Policy and Finance Committees. This Joint Committee was against increasing the membership subscription, but it recommended that the price of *The Analyst* and *Analytical Abstracts* be increased in 1957 to 5 guineas.

The whole question of finance had to be reconsidered once again, however, towards the end of the year, owing to a subsequent considerable increase in the cost of printing and also of a threat of further increases in the future. It has now been decided by Council that from January 1st, 1957, the price of *The Analyst* and *Analytical Abstracts* to outside subscribers shall be increased to 6 guineas, and the price of copies of *Analyatical Abstracts* that are sold separately correspondingly increased.

The Council has also decided that it will be necessary to increase the subscription of members of the Society. This step has been taken with some reluctance, but it is realised that only by this means can the continued existence of the Society be ensured. In this connection two main points must be borne in mind. Firstly, the membership subscription includes the two journals, *The Analyst* and *Analytical Abstracts*, and, moreover, the cost of producing these journals steadily increases year by year. Secondly, the activities of the Society increase year by year. All new activities of the Groups and Sections are available to all members without additional subscription, and the efficient organisation of these activities has required additions to our headquarters staff. Apart from these factors, we must look to the future and now that our journals are subsidised by grants our only means of building up reserves for future special activities is by subscriptions. It is with these facts in mind that the Council have come to the decision that as from 1957 the subscription shall be raised to 3 guineas per annum.

THE ANALYST—The 1955 volume contained 912 pages, compared with 792 in 1954. The numbers of papers and notes published in 1955 were 103 and 49, respectively, against 100 and 48 in 1954. Of the papers, three were lectures delivered at Special Meetings of the Society and two were Review Papers. After allowing for all matter other than papers and notes and for these five special papers, the average length of a paper or a note is 5·05 pages. This is an increase of half a page over the corresponding figure for 1954 and suggests that

the style of writing could well be made more concise. Summaries of fifteen papers presented at meetings but not being published in full in any journal were printed in the Proceedings of the Society.

Ten issues of the Bulletin were distributed with *The Analyst* during the year; two of these were special issues devoted entirely to material issued by the International Union of Pure and Applied Chemistry.

The increase of 700 in the number printed of each issue, made at the beginning of 1955, has been amply justified by the continued expansion of the circulation; for 1956 the number has been raised to 6000.

ANALYTICAL ABSTRACTS—The second volume was completed in December, 1955, and contained 3556 abstracts occupying 468 pages as compared with 3190 abstracts and 392 pages in 1954. The number of journals abstracted has steadily increased, and it is now unlikely that any important papers escape abstracting. Arrangements have been made with Dr. Bussieff to supply us with abstracts from Moscow and with Dr. Saito to do the same from Japan. The arrangement with the S.C.I. for exchange of abstracts continues to work satisfactorily. The addresses of authors are being included for an experimental period beginning in January, 1956.

CHEMICAL COUNCIL—During the year the Chemical Council has again made grants to the Society for the publication of original papers and abstracts. The Council acknowledges with thanks the sums of £1400 for *The Analyst* and of £1200 for *Analytical Abstracts*. A new appeal now being made to Industry by the Chemical Council will include funds not only for original publications and the Chemical Society Library, but also for abstracts.

CONFERENCE OF HONORARY SECRETARIES—A meeting of the Honorary Secretaries of the Sections and Groups of the Society was held in May, 1955, on the same lines as that of the previous year. Again the meeting was highly successful.

STAFF—Mr. B. J. Walby, B.Sc., A.R.I.C., resigned the posts of Assistant Editor of *The Analyst* and of *Analytical Abstracts* at the end of April, 1955. Mr. N. C. Francis was appointed Assistant Editor of *The Analyst* and Mrs. H. I. Fisk, B.Sc., Assistant Editor of *Analytical Abstracts*.

K. A. WILLIAMS, *President*.
N. L. ALLPORT, *Honorary Secretary*.

Report of the Analytical Methods Committee 1955

It is now a year since the Analytical Methods Committee of the Society for Analytical Chemistry was reorganised on a new basis to permit its work to be expanded and expedited. The Report that follows gives a brief history of the Committee and reviews the progress that has been made during the past year; it is intended to issue similar progress reports annually. It will be appreciated that any reconstruction must necessarily take time but, nevertheless, substantial progress has been made.

The constitution of the Analytical Methods Committee is as follows—

CHAIRMAN: D. C. Garratt, B.Sc., Ph.D., F.R.I.C.
(*Boots Pure Drug Co. Ltd.*)

N. L. Allport, F.R.I.C.	*Analytical Consulting Chemist and Bacteriologist; Honorary Secretary of the Society*
A. J. Amos, B.Sc., Ph.D., F.R.I.C.	*Analytical and Consulting Chemist*
R. Belcher, D.Sc., F.Inst.F., F.R.I.C.	*University of Birmingham (Department of Chemistry)*
R. C. Chirnside, F.R.I.C.	*Research Laboratories of The General Electric Co. Ltd.*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist; Hon. Treasurer of the Society*
J. Haslam, D.Sc., F.R.I.C.	*Imperial Chemical Industries Ltd. (Plastics Division)*
D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.	*Analytical and Consulting Chemist*
T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C.	*Public Analyst*
J. R. Nicholls, C.B.E., D.Sc., F.R.I.C.	*Department of the Government Chemist*
A. A. Smales, B.Sc., F.R.I.C.	*Atomic Energy Research Establishment, Harwell*
K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.	*Analytical and Consulting Chemist; President of the Society*

SECRETARY: Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.

GENERAL REVIEW

HISTORY OF THE COMMITTEE—

The Society through its Analytical Methods Committee has always been recognised as being an admirably suitable body for the collaborative work required for preparing and promulgating standard and reference methods of analysis.

The first Committee was appointed by the Council of the Society in April, 1924, as The Standing Committee on Uniformity of Analytical Methods and continued under this rather lengthy title until April, 1935, when it was changed to the less cumbersome one under which it now operates. The work of the Committee, its Sub-Committees and panels has always been, and still is, carried out voluntarily by members who have full-time duties in their own spheres of work. The fact that the Sub-Committees and panels have managed to continue, even during the Second World War, carrying out collaborative work on a diversity of problems and publishing 50 Reports in all since 1927 is some indication of the importance they attach to the work in hand, and the Society owes them a very large debt of gratitude for the unstinting help that they give.

In the past, the secretarial duties were undertaken by a member of each committee, and because such work had, of necessity, to be fitted into their own limited free time, it was only natural that progress was sometimes slow. Therefore, when the Society became

a purely learned body for the promotion of analytical chemistry as a whole, the Committee came under review and emphasis was laid on the need for expediting the preparation and publication of standard methods. Some reports from existing Sub-Committees were nearing completion, new projects were awaiting implementation and, in particular, the "Bibliography of Standard Methods," published in 1949, required expansion into a complete collection of methods—a formidable task in itself.

APPEAL TO INDUSTRY—

It was clear that this large programme of work required a great deal more time than existing facilities allowed, however willing the helpers. So, at the end of 1954, Dr. D. W. Kent-Jones, then President of the Society, launched an Appeal to Industry for subscriptions to a fund devoted to the work of the Committee. It was proposed in the first place to establish a full-time paid Secretariat, the Secretary being reponsible both for the servicing of the Committee and all its technical Sub-Committees and for the collection, editing and publication of the volume of Standard Methods to supplement the Bibliography. It was also proposed, should the Fund permit, to award one or more Studentships or Scholarships for research on important analytical problems.

Such was the very gratifying and prompt response to the Appeal that it was evident that these proposals to help the needs of the Society in this important aspect of its work were welcomed by industry. Donations were received from 79 subscribers, including commercial and nationalised industries and trade associations. Of these, eight entered into seven-year Deeds of Covenant, three others guaranteed annual amounts for seven years and a further twenty-six promised sums for three years in the first instance. Many of the other subscribers have indicated that they will continue their support in order that the Committee should have a reasonable annual income to carry on its work. In 1955, £8800 was received, and the Committee has firm promises of £5700 for each of the years 1956 and 1957.

TRUST FUND—

A Trust Fund, called the Society for Analytical Chemistry Analytical Methods Trust Fund, has now been established with the moneys received. Mr. Justice Lloyd-Jacob, who has been a very good friend to the Society for some years, has very kindly consented to be an independent Trustee. The other four Trustees represent the Society, being Dr. K. A. Williams (President), Dr. D. W. Kent-Jones (Past President), Dr. J. H. Hamence (Honorary Treasurer) and Mr. N. L. Allport (Honorary Secretary). Thus for the first time, the Analytical Methods Committee becomes a financially independent unit within the Society. The text of the Deed of Trust is reproduced as Appendix I to this report.

APPOINTMENT OF THE NEW ANALYTICAL METHODS COMMITTEE: ITS FUNCTION AND POLICY—

With such initial support, the Committee was able to start its work of expansion without delay. The original Committee was reorganised, the personnel of the new Committee being limited to 12 (including the Officers of the Society) and being selected to represent a fair cross-section of the field of analytical chemistry. Dr. D. C. Garratt, who had been Honorary Secretary of the Committee since 1946, was invited to be Chairman of the new Committee and Dr. C. H. Tinker was appointed as its first paid Secretary in February, 1955. The first meeting of the Committee was held on February 2nd, 1955, to discuss its future functions and policy, which would be wider in scope than in the past, since authority had been given by Council for the Committee to exercise greater powers than before and to be responsible for its own complete administration as well as acting as a steering committee for the technical work of the Sub-Committees and panels.

In its capacity as a steering committee, it examines critically new projects, particularly to assess their value in the general field of analytical chemistry, and, on approving them, appoints Sub-Committees to investigate the best methods of analysis, since such methods are intended for reference purposes. It should be noted that the techniques recommended may involve the use of the most up-to-date equipment, which might not yet be available in every laboratory. All methods that are recommended will always be open to revision according to current requirements and research. It was agreed that Sub-Committees should not be permanent but should be disbanded when the projects covered by their terms of reference have been completed.

PROGRESS OF WORK—

It will be evident from the detailed reports of individual committees that substantial progress has been achieved during the year.

Secretariat—As was to be expected, the progress during the first few months was somewhat slow. Not only had the work of the existing Sub-Committees to be reviewed with adjustments in their constitutions, where necessary, to permit the scope of their work to be broadened to bring it into line with the present needs, but also the Secretariat had to be organised *ab initio* to meet the requirements of the work.

The Secretariat started modestly, consisting only of the Secretary; however, with the rapid increase in the volume of work during the year, more spacious accommodation was acquired and the personnel has now risen to three, a graduate having recently been engaged.

Analytical Methods Committee and its Sub-Committees—In all, 30 meetings of the Committee and its Sub-Committees and panels have been held during the year, of which 10 have been meetings of the Committee itself.

At present there are seven active Sub-Committees under the aegis of the Committee. These deal with the following subjects—

Meat Products
Metallic Impurities in Organic Matter
Essential Oils
Pesticides Residues in Foodstuffs
Trace Elements in Fertilisers and Feeding Stuffs
Vitamins
Direct Micro-determination of Oxygen in Organic Matter.

Except for the last-named, which is a new Sub-Committee, these committees are continuing the work started under the old Committee, but for the first two the scope of work has been broadened with a corresponding change in constitution.

Three reports have been prepared by their respective Sub-Committees and have been approved for publication, as follows—

Report	*Prepared by*
Estimation of Vitamin B_{12}	Vitamin-B_{12} Panel
Determination of Linalol	Essential Oils Sub-Committee
Determination of Small Amounts of Organic Chlorine in Solvent Extracts of Vegetable Matter	Pesticides Residues in Foodstuffs Sub-Committee.

The responsibility for the collection of the Standard Methods to supplement the Bibliography has now been assumed by the Committee itself and is no longer borne by a Sub-Committee. A general form of presentation of the text of the methods has been agreed and so far two groups of the methods recommended in published Reports of the Analytical Methods Committee—namely, Analysis of Soaps (five methods) and Assay of Poisons (six methods)—have been collated and edited to conform to this. These are now under review to ensure that they are in line with current practice.

Joint Committee on Analysis of Trade Effluents—In addition to the Analytical Methods Committee and its Sub-Committees, there is an extremely active Committee on Methods of Analysis of Trade Effluents, which was set up jointly in February, 1954, by the Society and the Association of British Chemical Manufacturers under the Chairmanship of Mr. H. N. Wilson. This Joint Committee was appointed to continue the work originally started by an Analytical Sub-Committee of the Association's Trade Effluents Committee.

The technical work of this Joint Committee is divided between four Panels and originally each Panel was responsible for its own secretarial administration, the Joint Committee acting as a steering and co-ordinating committee. Very soon after its establishment, the Secretariat of the Analytical Methods Committee assumed practically all the administrative and preliminary editing work of this Committee and its Panels and, as can be seen from the detailed progress report, this has become so voluminous that the greater part of the work of the Secretariat has been devoted to it during the last six or seven months. Although, strictly speaking, this work does not come directly under the aegis of the Analytical Methods Committee, the whole problem of the control of trade effluents is considered to be of such national importance and urgency that priority has been given to it in order to facilitate and expedite publication of the methods in *The Analyst*.

The preparation of methods has progressed rapidly and already the first three have been published (*Analyst*, 1956, **81**, 59), three more have been prepared for publication in March, 1956, and there are some 20 to 30 others that have been completed and are now in various stages between approval by the Joint Committee and final editing, thus ensuring a constant supply for publication for some months to come.

In all, 29 meetings of the Joint Committee and its Panels have been held since March, 1955.

Research Studentship—In the past, one of the difficulties of the Analytical Methods Committee has been to arrange for special investigations into certain fundamental problems that arise during the collaborative work of the Sub-Committees and that require the services of a full-time worker. Such investigations can seldom be conveniently undertaken by members of the Sub-Committee because they are already fully engaged in their own work. Because of the good financial start to the work of the Committee it was decided that part of the Trust Fund should be set aside at once to meet this need by instituting a Studentship for research purposes, to be known as "The Society for Analytical Chemistry Studentship."

In view of the difficulties experienced in making accurate determinations of trace elements in organic matter, since these may be lost during the initial destruction of the organic material, the Committee has agreed that this problem should become the first subject for research. Since the behaviour of an element during ashing and subsequent chemical procedures can be followed by radiochemical techniques, the efficiency (or otherwise) of a particular method can be assessed, and it was decided that this new approach to the problem would be a fitting subject for the research work to be undertaken. Accordingly, arrangements have been made, by courtesy of the Director of the Atomic Energy Research Establishment, Harwell, for this work to be carried out under the direction of Mr. A. A. Smales at that Establishment, and the first Research Studentship, valued at £900 to £1000 per annum for two years, has been awarded to Mr. T. T. A. Gorsuch, B.Sc., A.R.I.C., who takes up his appointment on April 1st, 1956.

EXPENDITURE—

The audited statement of accounts (see Appendix II) for the first nine months (February to October inclusive) shows an expenditure of £1715; the expenditure for November to January inclusive is about £700, making a total for the year of approximately £2400.

The expenditure for 1956 will be considerably greater and is likely to be at least £4000, the principal increases being due to increased salaries for the additions to the staff and to expenses in connection with the Research Studentship.

FUTURE WORK—

As will be evident from the following detailed reports of the individual committees, there is still plenty of work in hand for some time to come. However, there is no lack of proposals and requests for problems to be tackled, and already the Committee is faced with the question of priorities.

The collaboration with another organisation in the matter of analysis of trade effluents has proved so successful that exploratory talks have taken place with a view to collaboration with other organisations in other branches of the chemical industry. As a result, agreement has recently been reached with the Pharmaceutical Society for a Joint Committee to be set up to examine standard methods for the analysis of drugs and source materials that are either no longer official in the British Pharmacopoeia or in the British Pharmaceutical Codex, or are outside the scope of these two publications.

REPORTS OF SUB-COMMITTEES OF THE ANALYTICAL METHODS COMMITTEE

MEAT PRODUCTS SUB-COMMITTEE

CONSTITUTION—

H. G. Rees, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C. (*Chairman*)	*Oxo Ltd.*
S. Back, B.Sc., F.R.I.C.	*Crosse & Blackwell Ltd.*
Miss E. M. Chatt, B.Sc., F.R.I.C.	*British Food Manufacturing Industries Research Association*

C. D. Essex, A.R.I.C.	*Oxo Ltd.*
J. R. Fraser, B.Sc., A.C.G.F.C., F.R.I.C.	*Department of the Government Chemist*
S. M. Herschdoerfer, Ph.D., F.R.I.C.	*T. Wall & Sons Ltd.*
H. Amphlett Williams, Ph.D., A.C G.F.C., F.R.I.C.	*Public Analyst*

APPOINTED—May 25th, 1955, to succeed the Meat Extract Sub-Committee, the terms of reference having been broadened.

FIRST MEETING—June 27th, 1955.

NUMBER OF MEETINGS DURING THE YEAR—3.

TERMS OF REFERENCE—"(*a*) The determination of the meat content of products containing meat; (*b*) the determination of the constituents of meat and meat products.

NOTE—The term 'meat products' to include hydrolysed protein and, if found necessary, fish pastes."

PROGRAMME OF WORK—

1. The collection of data on nitrogen factors for all types of meat.
2. To investigate methods for the determination of starch.
3. To investigate the determination of yeast in order to ascertain the presence of yeast extract.

At all times, the Sub-Committee maintains liaison with the Food Standards Committee of the Association of Public Analysts.

PROGRESS OF WORK—

1. *Nitrogen factors*—The collection of data on nitrogen factors is in progress; the literature is being searched, manufacturers are being approached and individual members of the Sub-Committee are carrying out experimental work.
2. *Determination of starch*—Work not yet started.
3. *Determination of yeast*—Work not yet started.

METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

CONSTITUTION—

T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C. (*Chairman*)	*Public Analyst*
L. Brealey, B.Sc.	*Boots Pure Drug Co. Ltd.*
C. L. Hinton, F.R.I.C.	*British Food Manufacturing Industries Research Association*
E. I. Johnson, M.Sc., A.R.I.C.	*Department of the Government Chemist*
I. MacIntyre, M.B., Ch.B.	*Post-Graduate Medical School, University of London*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*
G. Taylor, O.B.E., F.R.I.C.	*Analytical and Consulting Chemist*
G. E. Willis, B.Sc., Ph.D., A.R.I.C.	*Imperial Chemical Industries Ltd. (Dyestuffs Division)*

APPOINTED—April 19th, 1955, to succeed the Metallic Impurities in Foodstuffs Sub-Committee, the terms of reference having been broadened.

FIRST MEETING—May 10th, 1955.

NUMBER OF MEETINGS DURING THE YEAR—5.

TERMS OF REFERENCE—"To investigate the determination of small quantities of metals in organic matter."

PROGRAMME OF WORK—

1. To investigate the molybdenum-blue method for the determination of arsenic.
2. To investigate methods for the destruction of organic matter to avoid loss or accretion of the metal being determined during the procedure.

3. To review, and revise if necessary, the method for lead published as a tentative recommended method by the earlier Sub-Committee (*Analyst*, 1954, **79**, 397).
4. To investigate methods for the determination of copper.

At all times, the deliberations of the relevant Commission of the Analytical Section of the International Union of Pure and Applied Chemistry are noted.

PROGRESS OF WORK—

1. *Molybdenum-blue method for arsenic*—Collaborative experimental work is already in progress; various reduction techniques are being investigated in relation to the subsequent spectrophotometric determination of the arsenomolybdate complex.

2. *Destruction of organic matter*—The various accepted methods of wet and dry combustion, together with their many modifications, are being investigated to ascertain the conditions affecting the loss, retention or accretion of the metal being determined.

As has already been recorded earlier in the General Review under "Research Studentship," this problem is considered of such importance to the analyst as to warrant special research being devoted to it.

3. *Method for lead*—Evidence, both in this country and from abroad, has shown that, although it has been favourably received, the published tentative method has some limitations and work has now started on its revision.

4. *Method for copper*—Work not yet started.

ESSENTIAL OILS SUB-COMMITTEE

CONSTITUTION—

W. H. Simmons, B.Sc., M.Inst.Pet., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
A. J. M. Bailey, B.Sc., M.P.S., F.R.I.C. (*Honorary Secretary*)	*W. J. Bush & Co. Ltd.*
J. F. Charpy	*Formerly of J. & E. Atkinson Ltd.*
C. W. Cornwell, M.Sc., F.R.I.C.	*A. Boake, Roberts & Co. Ltd.*
G. W. Ferguson, B.Sc., Ph.D., F.R.I.C.	*Analytical and Consulting Chemist*
D. C. Garratt, B.Sc., Ph.D., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
H. T. Islip, B.Sc., F.R.I.C.	*Colonial Products Laboratory, Colonial Office*
P. McGregor, B.Sc., A.H.-W.C., F.R.I.C.	*Department of the Government Chemist*
W. M. Seaber, B.Sc., F.R.I.C.	*Analytical and Consulting Chemist*
J. H. Seager, M.Sc., F.R.I.C.	*Yardley & Co. Ltd.*
G. E. Smith, B.Sc., F.R.I.C.	*Stafford Allen & Sons Ltd.*

APPOINTED—By the Committee on Uniformity of Analytical Methods (predecessor of the Analytical Methods Committee), August 21st, 1924.

FIRST MEETING—October 16th, 1924.

NUMBER OF MEETINGS DURING THE YEAR—1.

PROGRESS OF WORKS—A Report on "The Determination of Linalol in Essential Oils" has been approved by the Committee and Council for publication.

FUTURE PROGRAMME—On the completion of the specified programme of work the Sub-Committee was formally dissolved.

The following were recommended as subjects for future work—

Peroxide value
Ester determination
Tertiary alcohols (including citronellol)
Cineole - cresol tables (revision).

Pesticides Residues in Foodstuffs Sub-Committee

CONSTITUTION—

G. Taylor, O.B.E., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
G. L. Baldit, B.Sc., A.R.I.C.	*Plant Protection Ltd.*
E. D. Chilwell, B.Sc., F.R.I.C. (succeeded G. S. Hartley, D.Sc., on June 20th, 1955)	*Fisons Pest Control Ltd.*
H. Egan, B.Sc., Ph.D., D.I.C., F.R.I.C.	*Department of the Government Chemist (representing the Food Group, Society of Chemical Industry)*
B. A. Ellis, M.A., F.R.I.C.	*Department of the Government Chemist*
J. C. Gage, B.Sc., Ph.D., A.R.I.C.	*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*
R. A. E. Galley, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C.	*Colonial Products Laboratory, Colonial Office*
D. C. Garratt, B.Sc., Ph.D., F.R.I.C.	*Boots Pure Drug Co. Ltd.*

APPOINTED—February 4th, 1954, following a request by the Fungicide and Insecticide Research Co-ordination Service of the Agricultural Research Council.

FIRST MEETING—March 26th, 1954.

NUMBER OF MEETINGS DURING THE YEAR—4 (including 2 of the Working Party (*q.v.*) and 1 jointly with the Metallic Impurities in Organic Matter Sub-Committee).

TERMS OF REFERENCE—"To examine the present position in respect of methods of analysis of foodstuffs for residual traces of pesticides, as the first action of the Sub-Committee; and, further, if deemed desirable, to recommend for general acceptance methods of analysis now in use, or to develop or assist in the development of new methods of analysis or modifications of methods now in use."

PROGRAMME OF WORK—

1. To devise a method for the accurate and precise determination of small amounts of chlorine in solvent extracts of foodstuffs for the purpose of identifying the presence of chlorinated hydrocarbons.
2. To investigate extraction procedures, and methods for removing organic impurities and colour from the resulting solutions.
3. To investigate methods for the determination of organo-phosphorus compounds.

PROGRESS OF WORK—

1. *Determination of small amounts of chlorine*—For the purpose of this work a small Working Party was appointed, consisting of: G. Taylor, O.B.E., F.R.I.C. (*Chairman*); A. J. Feuell, B.Sc., Ph.D., A.R.I.C. (*Colonial Products Laboratory*); D. C. Garratt, B.Sc., Ph.D., F.R.I.C.; G. A. Sergeant, M.Sc., A.R.I.C. (*Department of the Government Chemist*).

This work has been completed and a Report on "The Determination of Small Amounts of Organic Chlorine in Solvent Extracts of Vegetable Material" has been approved for publication.

2. *Extraction procedure*—Collaborative experimental work is now being carried out by the same Working Party.

3. *Organo-phosphorus compounds*—Work not yet started.

Trace Elements in Fertilisers and Feeding-Stuffs Sub-Committee

CONSTITUTION—

J. H. Hamence, M.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
D. C. Garratt, B.Sc., Ph.D., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
E. I. Johnson, M.Sc., A.R.I.C.	*Department of the Government Chemist*
R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.	*Analytical and Consulting Biochemist*

R. L. Mitchell, B.Sc., Ph.D., F.R.I.C.	*Macauley Institute for Soil Research (Department of Spectrochemistry)*
A. A. Smales, B.Sc., F.R.I.C.	*Atomic Energy Research Establishment, Harwell*
C. Whalley, B.Sc., F.R.I.C.	*Paint Research Station*

APPOINTED—February 4th, 1954.

FIRST MEETING—March 30th, 1954.

NUMBER OF MEETINGS DURING THE YEAR—None.

TERMS OF REFERENCE—"To devise appropriate methods of analysis (to be recommended for inclusion in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926) for the determination of the trace elements manganese, copper, zinc, cobalt, molybdenum, iodine, selenium and fluorine, and also for boron, magnesium and iron, which can be expected to be present in fertilisers in small quantities as distinct from traces."

PROGRAMME AND PROGRESS OF WORK—The terms of reference indicate the scope of the work and it is intended that methods should also be devised for feeding stuffs in appropriate cases. It is also intended to collaborate in a general revision of the methods of analysis at present prescribed in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926.

Samples of typical materials, with added known amounts of trace elements, have been circulated to selected members of the Sub-Committee for preliminary exploratory work, in which both physical and chemical techniques are being used.

VITAMINS

When the new Committee reviewed the work of the various Sub-Committees, it was decided not to recall the Vitamins Sub-Committee but merely to allow the work of the two existing Panels—on vitamin B_{12} and vitamin E—to be completed. For this reason, only the details of these two Panels are given below.

Vitamin-B_{12} Panel

CONSTITUTION—

A. J. Amos, B.Sc., Ph.D., F.R.I.C. (*Chairman*)	*Analytical and Consulting Chemist*
F. Wokes, B.Sc., Ph.D., F.P.S., F.R.I.C. (*Honorary Secretary*)	*Ovaltine Research Laboratories*
W. F. J. Cuthbertson, B.Sc., Ph.D., F.R.I.C.	*Glaxo Laboratories Ltd.*
J. E. Ford, B.Sc., Ph.D.	*National Institute for Research in Dairying*
F. W. Norris, D.Sc., A.R.C.S., D.I.C., F.R.I.C.	*University of Birmingham (Department of Applied Biochemistry)*
S. A. Price, B.Sc.	*Vitamins Ltd.*
G. E. Shaw, B.Sc.	*Evans Biological Institute*
R. E. Stuckey, B.Sc., Ph.D., F.P.S., F.R.I.C.	*British Drug Houses Ltd.*
G. Sykes, M.Sc., F.R.I.C.	*Boots Pure Drug Co. Ltd.*

APPOINTED—February 24th, 1953. An *ad hoc* Advisory Panel met on April 23rd, 1953. As a result of its recommendations, the Panel was appointed as above.

FIRST MEETING—December 7th, 1953.

NUMBER OF MEETINGS DURING THE YEAR—2.

PROGRESS OF WORK—The Panel has completed its work and a Report on "The Estimation of Vitamin B_{12}" is being published in March, 1956. The Panel has now been disbanded.

Vitamin-E Panel

CONSTITUTION—

A. L. Bacharach, M.A., F.R.I.C. (*Chairman*)	*Glaxo Laboratories Ltd.*
J. Green, B.Sc., Ph.D., A.R.I.C. (*Honorary Technical Secretary*)	*Vitamins Ltd.*
A. R. Moss, B.Sc., Ph.D.	*Roche Products Ltd.*
H. N. Ridyard, B.Sc., A.K.C., F.R.I.C.	*Research Association of British Flour Millers*

P. W. Russell Eggitt, B.Sc., A.R.I.C.	*Spillers Ltd.*
C. A. Shacklady, B.Sc., A.R.I.C.	*J. Bibby & Sons Ltd.*
P. Stross, B.Sc.	*British Drug Houses Ltd.*
G. Walley, B.Sc., F.R.I.C.	*Unilever Ltd.*
R. J. Ward, B.Sc., A.R.I.C.	*The Dunn Nutritional Laboratory, Medical Research Council*
E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.	*Analytical and Consulting Chemist*
F. Brown, M.Sc., Ph.D.*	*Christie Hospital and Holt Radium Institute, Manchester*
P. Harris, Ph.D.*	*Distillation Products Industries, Rochester, New York, U.S.A.*

* Corresponding member.

APPOINTED—March, 1953. An *ad hoc* Advisory Panel met on May 8th, 1953, to consider the need for standardising methods of vitamin-E estimation. As a result of its recommendations, the Panel was appointed as above.

FIRST MEETING—December 9th, 1953.

NUMBER OF MEETINGS DURING THE YEAR—5.

TERMS OF REFERENCE (OF ADVISORY PANEL)—"To survey the methods already proposed for the estimation of vitamin E and to recommend to the [Vitamins] Sub-Committee a standard method or methods."

PROGRAMME OF WORK—It was decided to consider only chemical methods for estimating tocopherols, collectively and individually, in food and feeding stuffs. A study of the method of Emmerie and Engel, with recent modifications involving chromatographic separation, was therefore undertaken.

PROGRESS OF WORK—As a result of collaborative experimental work, the Panel believes that a method for the determination of α-tocopherol can be recommended and a draft method is now under consideration. A draft of a general introduction to the whole report is also in hand.

Work continues on elaborating this method for the differential determination of any or all of the seven known tocopherols.

DIRECT MICRO-DETERMINATION OF OXYGEN IN ORGANIC MATTER SUB-COMMITTEE

This Sub-Committee was set up as a result of a proposal by the Microchemistry Group of the Society to carry out collaborative experimental work on the Unterzaucher method for the determination of oxygen.

CONSTITUTION—

D. W. Wilson, M.Sc., F.R.I.C. (*Chairman*)	*Sir John Cass College (Department of Chemistry)*
G. C. Ackroyd, B.Sc., A.R.I.C.	*D.S.I.R., Fuel Research Station*
P. R. W. Baker, B.Sc., A.R.I.C.	*Wellcome Research Laboratories*
Miss B. B. Bauminger, Ph.D., A.R.I.C.	*Dunlop Research Centre*
W. T. Chambers, B.Sc., Ph.D., A.R.I.C.	*British Rubber Producers' Research Association*
A. F. Colson, B.Sc., Ph.D., F.R.I.C.	*Imperial Chemical Industries Ltd. (Alkali Division)*
Miss M. Corner, B.Sc., F.R.I.C.	*D.S.I.R., Chemical Research Laboratory*
R. R. Gordon, Ph.D.	*National Coal Board, Central Research Establishment*
G. Ingram, A.R.I.C.	*Courtaulds Ltd.*
F. J. McMurray	*Wellcome Chemical Works*
F. H. Oliver	*Courtaulds Ltd.*
H. J. Warlow	*D.S.I.R., Fuel Research Station*
C. Whalley, B.Sc., F.R.I.C.	*Paint Research Station*

APPOINTED—June 28th, 1955.

MEETINGS—No meetings have yet been held, the preliminary work being conducted by post.

PROGRAMME OF WORK—To investigate the Unterzaucher method, and its modifications, for the micro-determination of oxygen.

PROGRESS OF WORK—Four samples of organic substances have been circulated to the Sub-Committee for collaborative experimental tests, each member employing his or her own version of the method. Detailed report forms have also been circulated and a number of these have now been returned to the Secretary for collation, before discussion at the first meeting.

REPORT OF THE A.B.C.M. - S.A.C. JOINT COMMITTEE ON THE ANALYSIS OF TRADE EFFLUENTS

CONSTITUTION—

Representing The Association of British Chemical Manufacturers—

H. N. Wilson, F.R.I.C.* (*Chairman*)	*Imperial Chemical Industries Ltd.* (*Billingham Division*)
J. G. Maltby, B.Sc., F.R.I.C.* (*Secretary*)	*Distillers Co. Ltd.*
F. G. Broughall, B.Sc., F.R.I.C.	*Midland Tar Distillers Ltd.*
D. C. Garratt, B.Sc., Ph.D., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
I. S. Wilson, M.Sc., Ph.D., A.R.I.C.	*Monsanto Chemicals Ltd.*

Representing The Society for Analytical Chemistry—

J. H. Hamence, M.Sc., Ph.D., F.R.I.C.*	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.	*Mersey River Board*
C. J. Regan, B.Sc., F.R.I.C.	*Formerly Chemist-in-Chief, London County Council*
J. G. Sherratt, B.Sc., F.R.I.C.	*Public Analyst and Consulting Analytical Chemist*
K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.	*Analytical and Consulting Chemist*
N. T. Wilkinson, F.R.I.C.	*Imperial Chemical Industries Ltd.* (*Alkali Division*)

J. S. Evans	*Federation of British Industries*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.*	*Secretary to the Analytical Methods Committee*

* Members of the Publication Sub-Committee, to which J. B. Attrill, M.A., F.R.I.C., Editor of *The Analyst*, has been co-opted.

APPOINTED—As a Joint Committee by the Society and by the Association of British Chemical Manufacturers, February 17th, 1954.

FIRST MEETING—March 19th, 1954.

NUMBER OF MEETINGS DURING THE YEAR—11 (including 5 of the Publication Sub-Committee).

TERMS OF REFERENCE—"To devise and recommend methods of analysis as applied to trade effluents, specifying in each case their applicability and limitations, but not the interpretation of the results of such tests as would be used to decide on the quality of an effluent. Such methods would be published by the Society as Recommended Methods."

PANEL 1: ORGANIC MATTER—GENERAL

CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C. (*Chairman*)	*Formerly Chemist-in-Chief, London County Council*
G. S. Clements, A.R.C.S., F.R.I.C. (*Secretary*)	*Public Health Department, London County Council*
W. M. Cameron, M.Inst.S.P., F.R.I.C.	*Main Drainage Department, Middlesex County Council*

W. T. Lockett, M.Sc.	*Main Drainage Department, Middlesex County Council*
T. B. Moore, B.Sc.	*North Thames Gas Board*
A. E. J. Pettet, B.A.	*D.S.I.R., Water Pollution Research Laboratory*
I. S. Wilson, M.Sc., Ph.D., A.R.I.C.	*Monsanto Chemicals Ltd.*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.	*Secretary to the Analytical Methods Committee*

FIRST MEETING—March 31st, 1954.

NUMBER OF MEETINGS DURING THE YEAR (AS FROM MARCH 1ST, 1955)—5.

PROGRAMME OF WORK—

Methods for determining oxygen demand—(*a*) general considerations; (*b*) permanganate value (oxygen absorbed from permanganate); (*c*) biochemical oxygen demand; (*d*) dichromate value (oxygen absorbed from boiling dichromate).

Methods for determining combined nitrogen—(*a*) free and saline ammonia; (*b*) albuminoid nitrogen; (*c*) organic nitrogen; (*d*) total unoxidised nitrogen; (*e*) nitrogen as nitrite; (*f*) nitrogen as nitrate.

Methods for determining total organic carbon.

Methods for determining phosphorus.

Methods for determining chloride ion (*chlorion*).

To list inhibitory substances, present in some trade effluents, which may interfere in any of the recommended methods.

PROGRESS OF WORK—

Work completed—Methods for determining the following have been passed to the Main Committee for approval: permanganate value; dichromate value; chlcride ion (chlorion); organic carbon.

Work in hand—Draft methods for determining the following are nearing completion: (*a*) the various forms of combined nitrogen; (*b*) biochemical oxygen demand; (*c*) phosphorus.

PANEL 2: METALLIC CONTAMINANTS

CONSTITUTION—

N. T. Wilkinson, F.R.I.C. (*Chairman*)	*Imperial Chemical Industries Ltd.* (*Alkali Division*)
D. C. Garratt, B.Sc., Ph.D., F.R.I.C.	*Boots Pure Drug Co. Ltd.*
J. H. Hamence, M.Sc., Ph.D., F.R.I.C.	*Public Analyst, Official Agricultural Analyst and Consulting Chemist*
J. G. Sherratt, B.Sc., F.R.I.C.	*Public Analyst and Consulting Analytical Chemist*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*

FIRST MEETING—September 10th, 1954.

NUMBER OF MEETINGS DURING THE YEAR (AS FROM MARCH 1ST, 1955)—6.

PROGRAMME OF WORK—

Preliminary treatment of sample. Methods for determining aluminium, antimony, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, sulphate, titanium and zinc.

PROGRESS OF WORK—

Work completed—The following methods were published during the year (*Analyst*, 1956, **81**, 59): Preliminary treatment of sample (destruction of organic matter); determination of arsenic; determination of copper.

Methods for determining the following have been prepared for publication in March, 1956: iron, mercury and nickel.

Methods for determining the following have been passed to the Main Committee for approval: chromium, lead and selenium.

Work in hand—The final draft method for manganese is being prepared. Work is proceeding on methods for zinc and silver, and methods for other metals and sulphate are being considered.

PANEL 3: NON-METALLIC CONTAMINANTS

CONSTITUTION—

F. G. Broughall, B.Sc., F.R.I.C. (*Chairman*)	*Midland Tar Distillers Ltd.*
W. G. Carey, F.R.I.C.	*Public Analyst and Official Agricultural Analyst; Consultant*
G. U. Houghton, M.Sc., Ph.D., F.R.I.C.	*South Essex Waterworks Co.*
E. A. W. Whitlock, B.Sc., A.R.I.C.	*Wallace & Tiernan Ltd.*

MEETINGS—The Panel has not met; so far its work has been conducted by post.

PROGRAMME OF WORK—Methods for determining free chlorine, cyanide, fluorine, formaldehyde, phenols, sulphide, sulphite, thiocyanate and thiosulphate.

PROGRESS OF WORK—Methods for determining phenols and sulphide are in draft.

PANEL 4: PHYSICAL TESTS

CONSTITUTION—

J. G. Sherratt, B.Sc., F.R.I.C. (*Chairman*)	*Public Analyst and Consulting Analytical Chemist*
L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.	*Mersey River Board*
G. A. Vaughan, A.R.I.C.	*Coal Tar Research Association*
K. A. Williams, B.Sc., Ph.D., A.Inst.P., M.Inst.Pet., F.R.I.C.	*Analytical and Consulting Chemist*
Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C. (*Secretary*)	*Secretary to the Analytical Methods Committee*

FIRST MEETING—May 11th, 1954.

NUMBER OF MEETINGS DURING THE YEAR (AS FROM MARCH 1ST, 1955)—8.

PROGRAMME OF WORK—

Method of sampling. Measurement of colour, transparency, temperature and pH. Determination of suspended solids, settleable solids, dissolved solids, immiscible liquids such as oil or tar, hardness (total hardness, calcium hardness and magnesium hardness), acidity and alkalinity.

PROGRESS OF WORK—

Work completed—The following methods have been passed to the Main Committee for approval: method of sampling; general description; measurement of colour, temperature, transparency and pH; determination of suspended solids, settleable solids, residue on dissolved solids and matter extractable by light petroleum.

Work in hand—Work is proceeding on methods for the determination of acidity, hardness and immiscible volatile liquids.

February 14th, 1956

APPENDIX I

TEXT OF THE DEED OF TRUST

THIS DEED OF TRUST is made the first day of February One thousand nine hundred and fifty six BETWEEN THE SOCIETY FOR ANALYTICAL CHEMISTRY whose registered office is situate at 7/8 Idol Lane E.C.3 in the City of London (hereinafter called "the Society") of the one part and THE HONOURABLE SIR GEORGE HAROLD LLOYD-JACOB of Fredley Manor Mickleham in the County of Surrey and DOUGLAS WILLIAM KENT-JONES of 18 Welsby Court Eaton Rise W.5. in the County of London and KENNETH ALAN WILLIAMS of 11 St. Dunstan's Avenue W.3. in the County of Middlesex and JACK HUBERT HAMENCE of 43 Westland Drive Hayes in the County of Kent and NOEL LIONEL ALLPORT of 325 Kennington

Road S.E.11 in the County of London (hereinafter together called "the Trustees" which expression shall where appropriate include the Trustees or Trustee for the time being hereof) of the other part———————————————

WHEREAS

(1) The Society is an association not for profit and was in the year One thousand nine hundred and seven registered under the Companies Acts 1862 to 1900 as a company limited by guarantee and not having a share capital The principal objects of the Society are to encourage assist and extend the knowledge and study of analytical chemistry and of all questions relating to the analysis nature and composition of natural and manufactured materials generally and to promote or assist to promote the efficiency and the proper administration of the laws relating to the control and composition of such materials generally and to take any steps which may be considered advisable for advancing or protecting the interests of analytical chemistry———————————

(2) The Society being desirous of establishing such a charitable trust as herein appears has caused to be transferred into the joint names of the Trustees the investments and cash (herein together called "the Initial Fund") particulars whereof are set out in the Schedule hereto to the intent that the same shall be held upon the trusts and with and subject to the powers and provisions herein declared and contained concerning the same (3) It is apprehended that further moneys investments and property may hereafter be transferred to the Trustees as an accretion to the Initial Fund———————————

(4) The Society has from among its members formed a Committee called and hereinafter referred to as "the Analytical Methods Committee" for the purpose of advising the Trustees on all matters concerning the allocation and application of the Trust Fund

NOW THIS DEED WITNESSETH and it is hereby agreed as follows:—

1. THE Trustees shall hold the Initial Fund and all such further moneys investments and property as may from time to time be transferred or paid to the Trustees as an accretion thereto (as and when the same shall be received) and the investments and property from time to time representing the same upon the trusts and with and subject to the powers and provisions hereinafter contained———————————

2. THE Initial Funds and such moneys investments and property as aforesaid and the investments and property from time to time representing the same (hereinafter collectively called "the Trust Fund") shall constitute a fund to be known as "the Society for Analytical Chemistry Analytical Methods Trust Fund"———————————

3. THE Trustees shall hold the Trust Fund upon trust subject to the provisions of the next succeeding Clause hereof to apply the capital and income thereof in such manner as the Trustees shall think fit in promoting and encouraging the acquisition and dissemination of knowledge in regard to methods of chemical analysis the study and improvement of methods of chemical analysis and the education of persons as analytical chemists———————————

4. THE Trustees shall out of the Trust Fund pay all costs and expenses of or incidental to the preparation and execution of these presents and the transfer to the Trustees of the investments comprised in the Initial Fund and the costs charges and expenses of the Trustees in or about the management of the Trust Fund and the execution of the trusts and powers upon and subject to which the same is held———————————

5. WITHOUT prejudice to the generality of the powers conferred upon them by Clause 3 hereof it is hereby declared that the Trustees may for the purposes of exercising such powers:—

(a) establish and maintain a Secretariat and staff to work under the direction of the Analytical Methods Committee and Sub-Committees and panels thereof and may under the like direction organise such research and other activities as may be expedient to discover and publish particulars of standard or approved methods of analysis

(b) provide or assist in providing all necessary means including books instruments plant equipment and chemical and other materials for the pursuit of research and

investigation into all matters relating to the development and establishment of methods of analysis

(c) establish and maintain bursaries scholarships studentships and grants-in-aid for the benefit of students of and workers in any college university or other laboratories in which the study of analytical chemistry is pursued

(d) establish and maintain studentships to be called "the Society for Analytical Chemistry Studentships" of such annual value as the Trustees may from time to time determine to be awarded in manner hereinafter mentioned to students of and workers in any college or university or other laboratories in which the study of analytical chemistry is pursued and to be held and enjoyed as hereinafter provided

(e) establish and maintain a scholarship or scholarships to be called "the Society for Analytical Chemistry Scholarships" of such value as the Trustees may from time to time determine and such scholarships shall be awarded to such persons and be held and enjoyed as hereinafter provided

(f) establish or maintain or assist in establishing or maintaining a chair or professorship for the advancement of analytical chemistry at any university teaching hospital or place of learning in the United Kingdom

(g) develop organise enter into and carry out or co-operate in any scheme or schemes which is or are calculated to further the objects of the Trust Fund——————

6. ANY such studentships or scholarships as aforesaid shall be awarded at such intervals to such persons and in such manner and shall be held and enjoyed for such period and upon and subject to such terms and conditions as shall from time to time be determined by regulations to be made by the Trustees in consultation with the Analytical Methods Committee and the Trustees may at any time revoke or alter any regulations made under the provisions of this clause and make new regulations in the place thereof——

7. THE Trustees may invest so much of the Trust Fund as shall not be immediately required in any investments permitted by law for the investment of trust money or any investments which at the time of investment are officially quoted on the Stock Exchange London Provided that no investment shall be made in the shares or securities of any company the paid up capital of which at the time of investment is less than five hundred thousand pounds or its equivalent in the currency of the place of registration of such company with power for the Trustees to vary such investments for others of any nature hereby authorised——————————————————

8. THE statutory power of appointing a new Trustee or new Trustees hereof shall apply

IN WITNESS whereof the Society has caused its common seal to be affixed and the Trustees have set their respective hands and seals the day and year first above written

SCHEDULE

£100 Ceylon Government 3¼% Stock 1959
£100 3½% Conversion Stock
£100 3½% War Stock
£6000 Cash

The Deed of Trust was signed and sealed on behalf of the Society by the President, Dr. K. A. Williams, the Honorary Secretary, Mr. N. L. Allport, and Messrs. J. R. Leech, L. Hinton and H. W. Hodgson, and signed and sealed by the Trustees, The Honourable Sir George Lloyd-Jacob, Dr. D. W. Kent-Jones, Dr. K. A. Williams, Dr. J. H. Hamence and Mr. N. L. Allport.

APPENDIX II

INCOME AND EXPENDITURE ACCOUNT OF THE ANALYTICAL METHODS COMMITTEE FROM FEBRUARY 1ST, 1955, TO OCTOBER 31ST, 1955

	£		£
Rent, Light, Heat and Telephone ..	49	Donations received January 1st to October 31st from Industry as result of Appeal	8794
Salaries	1198		
Office Equipment	232		
Other Expenses, including Printing and Stationery	236		
Balance Carried to Balance Sheet ..	7079		
	£8794		£8794

APPENDIX III

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The Fourth Bernard Dyer Memorial Lecture

The Evolution of Agricultural Research

By SIR WILLIAM SLATER, K.B.E.

(*Delivered after the Annual General Meeting of the Society, February 29th*, 1956)

When we meet to honour a great man, we can do so best by considering one of the qualities which marked him as outstanding amongst his fellows. Bernard Dyer had many admirable qualities, any one of which might form the subject of a lecture in his honour. In picking a subject, however, the lecturer must have in mind not only the quality he selects but also, if honour is truly to be paid, the need to show how those following in Dyer's footsteps may draw strength and inspiration from the study of this aspect of his life and work.

Before I decided on the subject of this lecture, I read again the admirable word picture of Dyer the man and of the work he did, painted by Sir John Russell in the first memorial lecture, knowing I should find there the inspiration I sought in picking a facet of Dyer's work which might enable me to say something not entirely unworthy of the occasion.

As I read, I became more and more impressed by Dyer's ability to grasp the essentials of a practical agricultural problem, to state it with great clarity and simplicity, and to apply his knowledge of chemistry to its solution. He did not speak in high-flown phrases of science for science's sake, nor did he enunciate his findings in terms intelligible only to his fellow scientists. Almost every investigation he undertook arose from the need to solve a problem of importance to agriculture, either one which he had set for himself or, more often, one which had been put to him by a group of farmers who were his clients. The results he obtained were stated with a simple clarity understandable to the intelligent layman, such as is achieved only by a small select band of gifted scientists. Yet in the work he was doing he was laying a large part of the foundation of modern soil chemistry. I hope to show how these qualities, whereby Dyer was able to serve faithfully the practical needs of agriculture, whilst at the same time so orientating his work that he achieved results of great basic importance, are called for in the planning and organisation of agricultural research as we know it to-day.

Perhaps the best way to begin is to ask the very simple and fundamental question: "What is agricultural research?" Whenever this question is asked, the answers tend to be varied and to be confused by the concept of agriculture as a science in its own right. Agriculture is not a science; it is an industry concerned with the growing of crops and the raising and care of stock. It is perhaps true that it is indeed, as is sometimes said, a "way of life," because to some men there is no other acceptable occupation, but essentially it is an industry, producing goods for sale and providing a livelihood for those working in it. Once this is accepted, the nature of agricultural research becomes simply the study by scientific method of the problems of agriculture. There is no scientific discipline which holds a special place in this work; it is a meeting ground of all the sciences, and each problem must be attacked by the men best equipped for its solution.

As in every other industry, the more the individual scientist knows of the industry he is serving the better able he will be to provide a solution to its problems. It is not, however, essential or even desirable that every worker should have a wide knowledge of agriculture; it is important that the problems he is called upon to solve should be stated to him clearly in terms which he can understand and which will enable him to appreciate their importance to the practical farmer. To do this, men are wanted with an intimate knowledge of agriculture and with a wide scientific training, to act as the interpreters between the laboratory and the production process. These men must be able to recognise and assess the problems that are facing the producer and to analyse these problems into their scientific components before they are put to the laboratory worker. They must be able to discuss the nature of the problem in scientific terms and be capable of understanding the method which the scientist proposes to use for its solution. At the same time, they should be sufficiently familiar with the broad outline of scientific progress to be able to suggest where the results of scientific work offer possibility of application in practice.

Finally, it should be their duty to study the best way in which new knowledge can be incorporated into commercial farming.

The task of these intermediaries clearly demands qualities rarely found in one man, and would be impossible were it not that many laboratory workers, by their knowledge of at least the aspect of agriculture related to their own work, can meet him more than half-way and that more and more farmers are receiving training which enables them to help in stating their problems in scientific language and in applying new knowledge on their farms.

It is entirely fallacious to believe that the work done by the intermediary between the laboratory and the field requires a lower order of intelligence than that needed in a laboratory worker. The idea that, provided a man has mud on his boots and can talk in a bluff, hearty way to farmers about their troubles and worries, he can fill this difficult role is nonsense. Contact between research workers and farmers as a whole has to pass first through the more intelligent and highly trained section of the farming population, and hence it is with this section the intermediary must be qualified to deal; to win their respect his scientific knowledge must be manifestly greater than their own. It is true he must know his farming well and he must have the gift of getting on with farmers and farm workers, but he must equally be a man with a high degree of intelligence and a scientifically trained mind and be endowed with more than an ordinary share of imagination.

The training and recruitment of men for this type of work is one of the major problems of agricultural research, and I shall return to it later.

When Bernard Dyer began his work in agricultural chemistry, farming, under the influence of Lawes and Gilbert and of Augustus Voelcker, was turning more and more to the chemist for advice and help. The science of chemistry was at the same time itself advancing rapidly, so that the small band of pioneer workers, engaged in applying chemistry to the solution of agricultural problems, had a wide range of knowledge and techniques available to them for use in their investigations. Before the First World War, fundamental knowledge in the major scientific disciplines continued to grow faster than it could be used by the workers then engaged in agricultural research. It seemed unlikely that the rate of application of the scientific facts and methods at their disposal would ever be fast enough to exhaust the store on which they drew.

From 1920 onwards, however, there was a great and rapid expansion in the number of workers engaged in agricultural research and in the facilities available to them. Much of this growth was stimulated by the farmers and horticulturists themselves; it was the logical sequence to the employment of the private consultant. In the next decade, many of our leading research institutes were founded and those already in being greatly expanded.

The major problems of agriculture were vigorously attacked by the exponents of many different scientific disciplines. Those for which a solution could be sought by the straightforward application of the knowledge and techniques already available were dealt with first and many notable and valuable results were achieved. There were, however, other problems of great practical importance which could not be solved by the direct application of the facts and methods already available to the workers. On some it was impossible even to make a start, whilst in others a promising beginning was made only for the workers to find themselves at a dead end; they could progress no farther until the immediate obstacle could be surmounted or an entirely new path of attack opened.

The character of agricultural research has, as a result, greatly changed in the last twenty years. Although scientific knowledge was advancing during this period more rapidly than ever before, it was obvious that the worker in agricultural research could not wait for someone else to provide the basic information he needed or to evolve the new technique without which he could not progress; he found that he himself must carry out investigations in fundamental science to forge the tools he wanted for his work.

In the period between the two World Wars, the recruits to agricultural research were mostly men trained in one of the basic sciences, who were drawn by an interest in agriculture to apply their knowledge and skill to the solution of its problems. They may at first have known little about farming methods, but they learned very quickly, as they brought a trained mind to work with enthusiasm and sympathy on the task to which they had been drawn.

With the increasing need for fundamental work, another type of recuit has come into the agricultural research service in increasing numbers, a man who is more attracted by a desire to seek scientific knowledge for its own sake than to solve the applied problems. He sees in a research institute the extensive facilities needed for much modern research and the opportunity to devote his time solely to the work in which he is interested, without

the distractions of teaching he would have in a university appointment. These men, joining the staff of an existing institute to work, say, in the field of biochemistry, may never get the understanding and sympathy for agriculture which is characteristic of the older workers who entered agricultural research to apply their knowledge to the solution of practical problems.

There is an advantage in having a number of workers concentrating on fundamental studies and not concerning themselves with the industry. Often the temperament and intellectual approach of a man capable of doing original work of this type are unsuited to applied research. This difference may be sometimes overstressed and the scientist working in a pure field may become a little "precious." It is, however, impossible to dispute that the difficulty of keeping in touch with the literature and developments in any single modern science makes it essential to have a number of men who concentrate on a science rather than on the broad problems of an industry.

There are, nevertheless, two aspects of the recruitment of these pure scientists which must be carefully watched. The first is the maintenance of the right balance between the different types of workers and the second the need to ensure that the workers and the work in the pure science subjects are of a kind and quality to justify the expenditure involved.

In many university departments there has been a growing tendency to encourage science graduates to look to pure rather than to applied research as a career. It has become almost a sign of failure if a graduate does not get a post-graduate award and stay at his university to work for a Ph.D. degree. The goal at which men are encouraged to aim is a career in pure research, with a long list of scientific publications and the Fellowship of the Royal Society as a final objective. No one would quarrel with the desirability of this goal, but few among the science graduates of our universities have the imagination, the determination and the intelligence to achieve it. Yet once a man has set out towards it, he finds a change of direction most difficult. Schooled to think of applied research as an inferior type of work, he must regard a change from pure research, in which he follows his own fancy in selecting a problem, to applied, in which his problems are provided for him, as a retrograde step. He often continues to struggle along the way he has chosen, vigorously and sometimes bitterly resenting any suggestion that he should change it, long after he has lost all inspiration and when his work has become dull and routine; pure only in that it has no foreseeable application.

As a result of this early indoctrination in the universities, many young men, joining the staff of one of the agricultural research institutes, consider it almost a right that they should continue to select their own problems, seeking knowledge for its own sake, but keeping a close eye on the personal reputation to be gained from a steady flow of published papers. Nor can they be blamed for this attitude to their work; the scales are heavily weighted in favour of a worker who makes even a moderate showing in this type of research.

When I graduated, just before the First World War, I consulted my professor about the career I should follow in chemistry, expressing a desire to undertake research with the hope of later finding a place on the staff of a university. I was fortunate in holding one of the very few post-graduate awards available and hence I felt in a position to contemplate this course. My professor agreed that I should try my hand at this very difficult game, but then went on to issue a warning. Only a few, he said, of those who started on a university career could ever hope to gain a university chair and the rest could look forward to a poor financial reward. I should, he explained, be gambling on having the necessary ability and luck to obtain one of the plums of the profession. If, on the other hand, I were prepared, after a year's training in research or in one of the branches of analytical chemistry, to go into industry or into a consulting practice, I might well, if I reached the top, earn more than a professor and, if I proved to have no more than average ability, a much better income than mediocrity received in a university. He mentioned no other openings than a university where a career in pure research could be followed for the good reason that there was virtually none.

Although to-day the biggest financial rewards are still to be obtained in the higher posts in industry, the average research worker is at least as well paid in a government research institute as he is in industry, and probably better. The system whereby a man receives regular increments and promotion, provided he works steadily and is competent, gives him certainty of earning a reasonable salary; whilst if he shows himself above average he can win more rapid promotion and a final salary roughly comparable with that of a corresponding

post in a university. In producing evidence of a man's contribution to scientific knowledge when he is to be considered for early promotion, it is much easier to make a case on the basis of published papers arising from fundamental studies than it is on work directed to the solution of applied problems, which may often be unsuitable for publication in a scientific journal. As a result, the man working on fundamental problems of his own selection has a somewhat better chance of early promotion.

Thus, both personal interest and financial advantage now weigh in favour of the choice of fundamental research, with the result that increasing numbers of workers in agricultural research wish to concentrate on this type of investigation. Of the men doing so, many are not able to maintain the flow of new ideas and self-engendered enthusiasm needed for success and, after a time, their work loses its value. They may still be very capable scientists, but they require a stimulus from without to keep them going at full pitch.

There has, therefore, perhaps been a tendency to get the work on agricultural research out of balance by favouring fundamental studies too much and by continuing to give encouragement to men on this class of work when they might be more usefully and happily employed on applied problems. We must, therefore, in the next few years, give careful consideration to this question of maintaining a correct balance between fundamental and applied work and find a means whereby those with real ability to evolve new principles and techniques and to seek the basic knowledge we need are permitted to do so and fully rewarded, whilst at the same time we encourage equally by suitable financial advancement the larger number of workers to concentrate on the solution of applied problems, to which they are more fitted.

We may draw confidence for such a course from a study of Bernard Dyer's work. He would, I am sure, never have claimed that he was doing more than solve problems for his clients, yet from his work has come most of our methods of soil analysis; to-day much of the work of this type is classed as fundamental research to be carried out only as a matter of personal inspiration. Surely we have given to much honest professional chemistry an air of mystic inspiration that is entirely unjustified. It would be just as reasonable to assume that the same qualities of mental exaltation were required to write a *Times* leader and, say, an ode of Keats. The one is produced, the other happens.

So far I have discussed only the problem of men, because it is much the most important, but even the most brilliant man must have a building in which to work and equipment to use. Since the war, there has been an alarming rise in the needs of all types of workers for apparatus and equipment. It is not the same apparatus that is costing more; it is an entirely new range of instruments that is called for. A new technique such as chromatography has its special demands; the centrifuge must now work faster and be refrigerated; there must be ultra-violet and infra-red spectrophotometers; and the humble hand calculating machine has given way to a complicated electrically operated machine, which in turn will soon be followed by an electronic computor. Whilst we may all be convinced of the need to give full financial support to research as the soundest investment the nation can make, the very high cost of equipment must make us think carefully to see that when it is provided it is fully and properly used and that we do not purchase some expensive gadget for no other reason than that a rival laboratory already has one and some day we may have a use for it.

The efficient use of expensive equipment raises a number of difficult issues. We may, for example, ask ourselves whether some pieces of equipment can be provided in more than one or two laboratories and hence whether work requiring their use should be concentrated there. The traditional approach to this problem has been to provide equipment whenever the work of an institute seemed fully to justify it. There must, however, be a limit to this, depending on the relative costs of the instrument and its servicing as compared with the salaries of the workers. Before the war, it rarely happened that a single instrument cost more than a fraction of the annual salaries then paid to those who were to use it, and called for little in the way of annual servicing.

Now is is not unusual to find a small group of scientists with total salaries of, say, £3500 per annum, who want an instrument or instruments for the further development of their work, costing £10,000 or more and requiring in the wages of technicians and other charges £2000 to £3000 per annum for its servicing. The same equipment may already be available in another laboratory financed from the same source. If it is, we must ask ourselves whether it is already fully used and, if not, whether the group now asking for duplicate equipment cannot also use it.

It may well be that the apparatus is so far used only for relatively short periods by the one group and could easily meet the needs of the other, but it is rarely possible to arrange for such co-operation. The second group is inevitably at the other end of the country, and even if they could be directed to move to the laboratory where the required apparatus is available, there are always a dozen reasons why this move cannot be made. The laboratory invariably has no space for their other work, which has to be carried on apart from the need for special apparatus. They will certainly require other expensive equipment which is only provided in the laboratory where they now are, and if the scientists can be moved the laboratory technicians certainly cannot. The last argument is unanswerable, because nowadays no scientist appears to be able to work without at least one technician with specialised training.

In agriculture, we have a difficult problem in providing large-scale facilities for work on farm animals, particularly where this involves the isolation of sick animals. The farming organisation to grow the food and manage the stock for large numbers of stall-fed animals is complex, and, unless it is highly efficient, the costs become prohibitive. Institutes for this type of work must of necessity be limited to one or two and be situated in the country, away from large urban populations; much of our veterinary research is carried out in universities and research institutes where the facilities for keeping animals under controlled conditions are limited and have to be shared between numbers of workers with many different interests. Investigations which it is not anticipated will call for many animals have a habit of developing, for their successful conclusion, the need for much larger numbers. The statement that "to obtain a statistically significant result two groups with not less than twenty (or may be thirty) animals in each will be required" is all too well known. But here again we have the problem of Mahomet and the Mountain, the worker responsible for the experiment cannot go to the animals and we cannot move the animals to the worker. Ideally, each worker should have the animals he requires provided near his laboratory, but, quite apart from the prohibitive cost of such a plan, it would be grossly wasteful, and often would be impracticable because the necessary land and staff were unobtainable.

So far no solution has been found to this problem, but it seems probable that in the end the worker, finding that the experimental farm and its animals are immovable, will decide that he must himself go to this particular mountain. All that can be done at present is to make this journey as easy as possible. The need to make it will continue to grow without our intervention if the cost of providing these facilities goes on rising more rapidly than the funds available.

A comparison of the programmes of research being undertaken before the war and now shows the great increase in the complexity of the work and the marked degree in which it is fragmenting into more and more separate and highly specialised branches. As an example of this development, the control of weeds in growing crops will serve well. For more than fifty years attempts have been made to use chemical sprays to kill weeds, whilst damaging the affected crops as little as possible; but up to the outbreak of the Second World War they had not progressed very far. Some success had been achieved, depending largely on differences in physical character between the crop and the weeds; thus onion crops were sprayed with sulphuric acid, which ran down the narrow, smooth vertical leaves but remained on the broad flat leaves of many of the invading weeds.

During the war chemists and plant physiologists in the laboratories of Imperial Chemical Industries at Jeallott's Hill, at the Rothamsted Experimental Station, and later at Oxford, studying the chemistry and mode of action of plant hormones, evolved the idea of using related substances as selective herbicides, and from this work has arisen the whole range of substituted phenoxyacetic acid compounds now widely used on our farms. These discoveries at the same time opened up a wide series of new problems for investigation. The chemist was concerned in the synthesis of different series of organic compounds related in structure to the substances known to affect plant growth in different ways. The biochemist and the plant physiologist were interested in the mode of action of these substances and in such questions as their translocation in the plant. A range of biological tests had to be developed for the study of the activity of growth-regulating substances, and of chemical tests to determine how long they took to disappear from the plant or the soil. The bacteriologist was involved in investigating the ways in which micro-organisms break down these compounds. New field techniques have had to be worked out by the botanist and statistician to measure the efficiency of the different herbicides in destroying weeds and their effect on the yield

and quality of the different crops in which the weeds were growing. The same team of workers had also to study the effects of treating crops and weeds at different stages of growth and the impact of such factors as the type of soil, the nutritional status of the crop, the crop variety and the local climatic conditions on the efficiency of the herbicide. With the help of a chemist, they had to study the formulation of the solutions used for spraying and how the different solvents and diluents affected the efficiency of the active compound.

The possibility of applying radioactive-tracer techniques to these problems meant that before long the chemists and physicists skilled in this work arrived with their specialised needs in laboratories and equipment. In the latest developments coming from the Agricultural Research Council Unit at Wye College, a study of the enzymic breakdown of non-toxic substituted phenoxybutyric and other phenoxyaliphatic acids to the toxic phenoxyacetic compounds has shown that it is possible to prepare compounds of specific molecular structure effective only against plants containing the enzyme system capable of reacting with them. The further exploitation of this concept must take us much further into the biochemistry of plant enzymes and all the related problems of plant growth.

This illustration from a small but important section of agricultural research serves to show how each part of the work is calling for an increasing number of specialists. It cannot be expected that all these men will be interested in practical farming and able to relate the small field in which they work to the broad general problems of agriculture. Many of the scientists required come from an urban background and until they join an Agricultural Research Institute they may have little or no knowledge of farming, let alone have given thought to its technical problems. It has been suggested that the institutes should recruit only men with a farming, or at least a country, background, but that is impossible. When a biochemist is needed with a good knowledge of, say, protein chemistry and capable of undertaking individual research, the field of selection is small enough, without imposing on it the further qualification of a rural upbringing. We should make very slow progress if we confined our efforts in this way.

As in the future our laboratories employ greater numbers of these specialised research workers, the need for men who can bridge the gap between them and the farmer becomes increasingly important.

I have already mentioned the work these men must do and the qualities required for this work and I want now to return to the consideration of the type of training they need; or, put another way, where we should look for possible recruits. The most obvious place is in the agricultural schools of the universities. An examination, however, of the courses of study followed for the agricultural degrees does not suggest that, in general, they will produce the type of man we need. The curriculum in agriculture attempts to cover an extremely wide range of subjects, so that the student's time is filled with attendance at lectures and practical classes. He must study chemistry, physics, botany and zoology, and the applied aspects of these sciences; he is required to learn something of economics, accounting, land agency and building construction; in addition, he must acquire knowledge of crop and animal husbandry, which includes such diverse subjects as the management of farm machinery and the care of sick animals. The curriculum is not the same in each university, but in most schools of agriculture all the above subjects are covered and in many there are others in addition, arising from the special interests of the staff. If the students entering the course were outstanding men, it would still be impossible to use such a wide range of subjects as the proper basis for training in scientific method. Agriculture is in most universities one of the few remaining pass-degree courses and unless a man is determined to follow it he will, if he has shown the necessary ability, tend to be diverted to an honours school. Although in doing so his tutors may be directing him wisely, the result is to drain away many of the best university entrants from agriculture. Whilst there are outstanding exceptions of men who have achieved distinction in research work after graduating in agriculture, it is true that most agricultural graduates have not the basic training in science to enable them to take up a research career. They cannot in the time at their disposal have mastered any one scientific discipline and they certainly cannot have spent the hours in the laboratory which alone can lead to a mastery of its techniques. Whilst the agricultural graduate may be well able to talk to the farmer about his problems and to draw the scientist's attention to them, he is unlikely to be able to appreciate the laboratory problems involved, or exactly how the specialist scientist is, or should be, attacking the problem. He is equally unlikely to keep closely enough in touch with academic work to be able to recognise the importance

to the farmer of a discovery made in the laboratory, when the specialised originator of the idea has not done so.

There are many openings for which the agricultural graduate is well qualified, but apart from the exceptional man, he is not suited to uphold the interests of agriculture in an institute increasingly staffed by specialists.

What is required is the type of man entering agricultural research before the Second World War who, as I have said earlier, did so because of a strong desire to apply his knowledge and skill in one of the basic sciences to the practical problems of agriculture. Some such men do come from farming stock; the small farms of Wales and Scotland have already provided us with many of our best men of this type. Such men need little training in agriculture. Others have been fired with a desire to help in food production, by reading or hearing of the vital importance to the world of a larger agricultural output, or by coming by chance on some interesting application of their science to an agricultural problem. This group of recruits must, if they are not to become narrow specialists, be given the opportunity to get a general knowledge of farming. One way is to send them to take a post-graduate course in agriculture, such as that given in Cambridge; the other is to ensure that when they first join a research institute they are given problems which will take them on to farms, where they will acquire a general knowledge of agriculture. It is surprising how quickly, for example, a chemist, if he is the right man, will pick up a good general knowledge of farming.

We need go no farther than the man we honour to-day and to your first Memorial Lecturer to find outstanding examples of chemists whose names will live long in the history of agriculture.

The National Agricultural Advisory Service provides a wider illustration of the value of this type of training and of how well it fits a scientist to act as intermediary between the laboratory specialist and the farmer. The specialist advisory officers in such subjects as soil and nutrition chemistry, entomology and plant pathology are recruited from men who have taken chemistry, botany or zoology as their first-degree subject. Some have followed this by taking the diploma in agriculture or that in agricultural science at Cambridge, but others, after a preliminary period of research training in a university, have been taken directly into the service. There they get every opportunity to visit farms in company with the district and county officers, who have been selected for their knowledge and experience in agriculture and horticulture. Within a remarkably short time the specialist officer picks up a general knowledge of the industry.

He can never know so much about the practical details of farming as his colleagues who have taken an agricultural degree, but he can apply his scientific knowledge and training to answer the unusual questions which arise on the farm. He may not be able to set a plough or milk a cow, but he can put the farmer right on the fertilisers to use or the rations to feed to stock, where traditional practice has broken down. There is no doubt that this group of scientists is highly respected and valued by the farmers.

At the same time their training enables them to talk freely and easily with the specialist worker in a research institute and to carry out themselves investigations generally of an applied character.

These men are clearly of the type required to form the bridge we are seeking to build, but they are too few in number and have too many other duties to complete it. What is needed is another span, formed of similar men based on the research institutes. There are still in our institutes many men with this training, and between them and the specialist advisory officers there is close co-operation. The proportion of research workers with a general knowledge of agriculture is, however, falling and, unless we make a conscious effort to increase it and make liaison with the Advisory Service a definite part of their duties, our span of the bridge may collapse.

All branches of agriculture are not equally well covered in the National Agricultural Advisory Service with scientifically trained specialists and in those where this scientific training is lacking lies the greatest danger of the laboratory and the farm parting company. The advisory officer not having a sound scientific training avoids contact with the scientist he does not understand and who does not understand him. The research worker, for his part, finding no response to proposals for the application of his specialised knowledge, tends to withdraw into his laboratory and concentrate more and more on fundamental research. It is in these branches that the research institutes will have to make the greatest efforts to find men with sound scientific training and a general knowledge of agriculture.

Looking into the future we see, therefore, two groups of men working together in the agricultural research institutes, both having their roots in the basic sciences, but applying their knowledge in different ways; the one group going ever deeper into specialised investigations in the laboratory and the other devoting itself to the immediate solution of the applied problems of the industry and maintaining contact with the Advisory Service and the farmers.

The qualities of Bernard Dyer of which I spoke at the beginning—his ability to grasp the essentials of a practical problem, to state it clearly and simply and to apply his knowledge of chemistry to its solution—are qualitites that will be called for more and more in the future development of agricultural research, and your Society is doing a service to the advancement of agriculture, which Dyer loved so much, by making us pause and think of what he did and what he stood for, when this Memorial Lecture is delivered.

Investigations into Methods of Determination of Lithium in Its Ores

By P. W. SYKES

Certain methods for the analysis of lithium ores have been examined and the errors in them determined. It is concluded that the most accurate method is the Berzelius attack followed by flame photometry.

The Lawrence Smith method[1] for the decomposition of silicate minerals and the isolation of the alkali metals as chlorides has, for many years, been used in the determination of lithium in its ores. It has been critically investigated by Kallmann[2] and other workers, but on the whole it has stood the test of time. The other classical method of decomposition of silicate ores is that of Berzelius,[3] but his has found little favour since the introduction of the Lawrence Smith method, because of difficulties in the chemical separations involved in the isolation of the alkali metals. It was, however, used by Bacon and Sparks[4] for the analysis of spodumenes, the lithium being determined by the periodate method, and by Ellestad and Horstman[5] in the determination of small quantities of lithium in silicate rocks, use being made of flame photometry.

Numerous methods of separating lithium from the other alkali metals have been proposed, but those based on the *iso*amyl alcohol method of Gooch[6] or the ether - ethanol methods of Rammelsberg[7] and of Palkin[8] appear to have been most widely used. The methods have been summarised by Forster.[9]

The flame photometer has permitted the determination of lithium in solution to be carried out with ease and accuracy and without the necessity for separating it from the other alkali metals. It has been used by Brumbaugh and Fanus[10] for the determination of lithium in spodumene, after attack on the ore by the Berzelius method.

The flame photometer has proved most useful for the determination of small quantities of lithium in residues that are normally discarded. With its aid both the Lawrence Smith and the Berzelius methods have been investigated as means for getting the lithium contents of ores into solution. In addition, the effectiveness of a conventional ether - ethanol method for the separation of lithium from the other alkali metals has been investigated.

Ores

The most important ores containing lithium, most of which have been examined in this investigation, are as follows—

Amblygonite	Li Al (F, OH) PO_4
Triphylite	Li (Fe, Mn) PO_4
Lepidolite	K Li Al_2 ($Al_2Si_3O_{10}$) (F, OH)$_2$
Zinnwaldite	K Li Fe Al ($AlSi_3O_{10}$) (OH)$_2$
Spodumene	Li Al (SiO_3)$_2$
Petalite	(Li, Na, H) Al (Si_2O_5)$_2$

The Lawrence Smith Method

The method used is briefly as follows. The ore is heated with a mixture of six parts of calcium carbonate and one part of ammonium chloride, and the sinter is cooled, digested with water and filtered. The water extract is acidified, boiled to remove carbon dioxide, and calcium is precipitated with ammonium hydroxide and ammonium carbonate. The solution is evaporated to dryness and the ammonium salts are removed by heating. The solid is dissolved in water acidified with hydrochloric acid, and traces of sulphate are precipitated by barium chloride. The solution is made alkaline again with ammonium hydroxide, excess of barium is removed with ammonium carbonate and any remaining calcium with ammonium oxalate. The filtrate is again evaporated to dryness and ignited to remove ammonium salts. The solid is dissolved in dilute hydrochloric acid, and the solution is filtered and again evaporated to dryness. The lithium chloride is then separated from the other alkali-metal chlorides, as described by Schoeller and Powell,[11] by extraction with a mixture of one part of absolute ethanol and 3 parts of diethyl ether. The filtrate is evaporated, sulphuric acid is added, and the residue is finally dried, ignited and weighed as lithium sulphate.

Flame Photometry

The E.E.L. flame photometer (Evans Electroselenium Ltd.) has been used throughout this investigation. The instrument has been described by Collins and Polkinhorne.[12]

The method used is as follows. Standardise the flame photometer (using a standard solution containing 15 parts of Li_2O per million) at a reading of 60 on the linear scale. Then spray into the flame the prepared unknown solution and take the reading. Repeat this procedure five times and average the readings. From a calibration graph obtained by spraying solutions of known concentration into the flame, the concentration of the unknown may be determined.

The standard deviation in the determination of the lithium content of a solution containing about 15 parts of Li_2O per million was determined experimentally to be about 5 parts in 1000, provided that the standard solution was sprayed into the flame before and after each determination of the unknown.

It has been found that the highest accuracy is obtained by using the centre portion of the instrument scale, and in most cases the concentrations of the unknown solutions were adjusted to give readings in this region.

Critical Examination of the Combined Lawrence Smith and Ether - Ethanol Method

Various reports have from time to time appeared that the lithium is nc completely liberated and rendered soluble in water by the Lawrence Smith attack, but it has always been considered that, if the extracted residue (consisting of calcium carbonate and the water-insoluble components of the decomposed ore) is completely soluble in concentrated hydrochloric acid, the attack is complete.

It was however found that, after 0·5 g of a finely ground sample of petalite had been heated with 3·5 g of Lawrence Smith mixture, in accordance with what had been the usual practice, a considerable quantity of lithium was not leached out of the sinter by water, although the leached residue fulfilled the condition of complete solubility in concentrated hydrochloric acid. Increasing the quantity of mixture to 7 g for 0·5 g of ore markedly increased the amount of lithium extracted. The increase in the amount from samples of other ores was small, as shown in Table I.

Table I

Determination of Li_2O in ores by combined Lawrence Smith and ether - ethanol method, different amounts of Lawrence Smith mixture being used

Ore	Li_2O found when 3·5 g of mixture used, %	Li_2O found when 7 g of mixture used, %
Amblygonite A	7·40, 7·35	7·45
Amblygonite B	8·48, 8·43	8·48
Lepidolite H	3·73, 3·71	3·77
Lepidolite J	3·75	3·75, 3·75
Petalite	3·42, 3·46	4·06, 4·08

But even with use of the increased amount of mixture, it has been shown that extraction of lithium is not complete. Eight water-insoluble residues from Lawrence Smith attacks (each with 7 g of mixture) on several samples of lepidolite were tested for residual lithium content. With every residue, a small but appreciable amount of lithium was extracted either by reheating the dried residue from the Lawrence Smith attack with ammonium chloride and re-extracting with water, or by dissolving the residue in hydrochloric acid and evaporating to dryness to precipitate silica. In each case the calcium was precipitated by ammonium carbonate, redissolved and reprecipitated before the lithium was determined in the solution. The smallest amount of lithium extracted corresponded to about 0·03 per cent. and the largest to 0·08 per cent. of Li_2O in the ore. Similarly, six residues from attacks on amblygonite have been examined and lithium has been found to be present in every analysis in amounts corresponding to 0·05 to 0·085 per cent. of Li_2O in the ore.

The fineness of grinding of the ore sample can also affect the amount of lithium rendered water-soluble by the Lawrence Smith attack. A sample of triphylite that had been ground through a 100-mesh sieve was analysed for lithium by the Lawrence Smith attack, followed by flame photometry. Values of 4·25 and 4·58 per cent. of Li_2O were obtained. The same sample after further grinding gave a value of 6·34 per cent. of Li_2O, and by the Berzelius attack followed by flame photometry, 6·43 per cent. of Li_2O.

PURIFICATION STEPS—

Two residues, which should be free from lithium, are rejected at the purification stage. The first consists of calcium carbonate, which has been redissolved and reprecipitated to ensure that it carries away no lithium. In fact, whenever such a residue was examined, the lithium content, although detectable, was quite insignificant. The second residue consists of barium sulphate, barium carbonate, calcium carbonate and calcium oxalate, and is quite small. Several such residues have been examined, and by redissolving (as far as possible) in acid and reprecipitating, lithium corresponding to between about 0·005 to 0·015 per cent. of Li_2O in the ore was extracted.

During this stage of the analysis, ammonium salts are twice removed by evaporation to dryness and ignition. The temperature of the material must barely reach a very dull red heat, or lithium chloride may be lost by volatilisation. In the second ignition the lithium may be partly present as lithium oxalate, and an incomplete extraction in the next stage will occur if this oxalate is not completely decomposed by heat. A temperature considerably above that required to volatilise the ammonium salts is necessary, but something less than a dull red heat is sufficient.

EXTRACTION OF LITHIUM—

The extracted residue—This should be free from lithium. Six residues from lepidolite analyses have been examined; lithium was detected in all. The amount was small (corresponding to between about 0·01 and 0·016 per cent. of Li_2O in the ore) except in one residue, with which the temperature of ignition in the purification stage was insufficient to decompose lithium oxalate, when the amount found was equivalent to 0·63 per cent. of Li_2O in the ore. With amblygonites, in which the ratio of lithium to other alkalis is very much higher, the lithium content of these residues was negligible.

The ether - ethanol extract—This should be free from all metals except lithium. A number of samples of the lithium sulphate directly derived from such solutions has been examined. The lithium, sodium and potassium present in each were determined by means of the flame photometer; the results of a fair selection of these are given in Table II.

In all cases small amounts of sodium and potassium are weighed and appear as Li_2O in the result of the analysis. Calcium also has been detected in the final lithium sulphate in small quantities by spectrographic examination, but the actual amount present has not been determined.

THE LAWRENCE SMITH ATTACK FOLLOWED BY FLAME PHOTOMETRY

INITIAL TREATMENT OF THE ORE—

Losses incurred by the failure of the Lawrence Smith procedure to extract the whole of the lithium from the ore have been described above. The following method was used for the determination by flame photometry of the lithium in the solution resulting from the

Lawrence Smith attack. Acidify the aqueous extract from the Lawrence Smith sinter with hydrochloric acid until just red to methyl orange, and make up to 500 ml. Heat 25 ml almost to boiling and add a 25 per cent. solution of ammonium carbonate dropwise until

TABLE II

DETERMINATION OF LITHIUM IN THE ETHER - ETHANOL EXTRACT

Ore	Equivalent Li_2O in ore: Accepted values from weight of Li_2SO_4, %	from flame-photometric determination of: lithium, %	sodium, %	potassium, %	Total of flame-photometric figures, %
Lepidolite G	3·97	3·88	0·042	0·021	3·94
Lepidolite H	3·93	3·88	0·042	0·017	3·94
Lepidolite J	3·75	3·73	0·024	0·015	3·77
Lepidolite K	3·32	3·35	0·038	0·023	3·41
Amblygonite C ..	9·07	8·98	0·035	trace	9·01

no more calcium carbonate is precipitated. Set aside for a few minutes, and then filter off the precipitate and wash it. Cool the solution and make it up to either 100 or 200 ml, depending on the expected Li_2O content of the ore. Use this solution for analysis by the flame photometer as described.

No clear evidence has been obtained that a significant loss of lithium occurs by the use of this procedure in place of the double precipitation of calcium carbonate normally used in the Lawrence Smith procedure.

INTERFERENCE OF OTHER ELEMENTS ON THE DETERMINATION OF LITHIUM BY THE FLAME PHOTOMETER—

A feature of the Lawrence Smith attack is the virtual absence from the leach solution of constituents of the ore other than the chlorides of the alkali metals and calcium. Since the last named is removed by precipitation before carrying out the determination, only the alkali metals have to be considered.

Sodium chloride does not interfere at any concentration investigated—the highest was about 100 times that normally obtained in a Lawrence Smith leach solution, and was over 30 times the Li_2O concentration.

The effect of potassium chloride is shown in Table III, and of rubidium chloride in Table IV.

TABLE III

EFFECT OF POTASSIUM CHLORIDE ON DETERMINATION OF LITHIUM BY FLAME PHOTOMETRY

Equivalent Li_2O present, p.p.m.	Potassium chloride added, p.p.m.	Equivalent Li_2O found, p.p.m.	Error, %
15	20	15·12	+ 0·8
15	40	15·16	+ 1·1
15	100	15·27	+ 1·8
15	200	15·32	+ 2·1
15	500	15·51	+ 3·4
0	40	~ 0·1	—
5	40	5·28	+ 5·6
10	40	10·30	+ 3·0
15	40	15·18	+ 1·2
20	40	20·10	+ 0·5

TABLE IV

EFFECT OF RUBIDIUM CHLORIDE ON DETERMINATION OF LITHIUM BY FLAME PHOTOMETRY

Equivalent Li_2O taken, p.p.m.	Rubidium chloride added, p.p.m.	Equivalent Li_2O found, p.p.m.	Error, %
15	20	15·05	+ 0·3
15	40	15·11	+ 0·7
15	100	15·18	+ 1·2

The potassium contents of a number of solutions from lepidolite analysis have been determined by means of the flame photometer; owing to the emission by rubidium of a red light fairly close in wavelength to that of potassium, the resulting figure includes a proportion of the rubidium. However, the composite figure was nearly constant for a number of different samples of lepidolite and is consistent with an ore content of about 9 per cent. of K_2O and 3 per cent. of Rb_2O, giving a solution for analysis containing about 10 p.p.m. of Li_2O, 35 p.p.m. of KCl and 10 p.p.m. of RbCl. From Tables II and III it will be seen that, as a result of the presence of the potassium and rubidium salts, the lithium content as determined by the flame photometer will be about 3 per cent. high. This error can be eliminated by including the appropriate concentration of potassium and rubidium chlorides in the standard with which the unknown solution is compared. Provided they are not too large, variations in the potassium and rubidium contents will not produce any serious error in the lithium determinations.

With amblygonite, which normally contains only very small quantities of alkalis other than lithium, no correction is necessary, provided that the calcium has been removed.

Berzelius attack followed by flame photometry

The details of the Berzelius attack are based on a method worked out by Messrs. Alfred H. Knight and are described later. Briefly, the ore is heated with hydrofluoric and nitric acids until it has dissolved. Ideally the whole of the constituents of the ore (with the exception of silicon, which escapes as silicon tetrafluoride) are obtained in solution, and are then converted to sulphates by reaction with an excess of sulphuric acid.

In practice, with lepidolite a small residue that stubbornly resists the attack is always found, and is presumably of different composition from the bulk of the ore. No trace of lithium has been detected in the solution resulting from the repeated extraction of this residue with hydrofluoric and sulphuric acids.

The solution containing the lithium as lithium sulphate is then analysed by flame photometry. Since practically the whole of the ore is obtained in solution, the possibility of the loss of lithium in the residue is excluded, and for this reason the method has much to recommend it, but the presence of the other constituents of the ore increases the possibility of error due to interference with the flame-photometric determinations.

Table V

Interference of aluminium

Equivalent Li_2O present, p.p.m.	Aluminium oxide added, p.p.m.	Concentration of sulphuric acid, *N*	Equivalent Li_2O found, p.p.m.	Error, %
10	0	0·32	9·65	− 3·5
10	20	0·32	9·65	− 3·5
10	40	0·32	9·65	− 3·5
10	60	0·32	9·7	− 3
10	80	0·32	9·65	− 3·5
10	100	0·32	9·7	− 3

Table VI

Interference of sulphuric acid

Equivalent Li_2O present, p.p.m.	Aluminium oxide added, p.p.m.	Concentration of sulphuric acid, *N*	Equivalent Li_2O found, p.p.m.	Error, %
10	60	0·0	10·05	+ 0·5
10	60	0·16	9·8	− 2
10	60	0·32	9·75	− 2·5
10	60	0·40	9·65	− 3·5
10	60	0·48	9·6	− 4
10	60	0·64	9·5	− 5
0	60	0·32	0	—
5	60	0·32	4·9	− 2
10	60	0·32	9·8	− 2
15	60	0·32	14·55	− 3
20	60	0·32	19·45	− 2·5
25	60	0·32	24·4	− 2·5

The interference due to the other alkali metals is mentioned above. That due to the other possible interfering substances is given in Tables V, VI and VII. All results are average of 5 readings.

TABLE VII

INTERFERENCE OF PHOSPHORIC ACID

Equivalent Li_2O present, p.p.m.	Equivalent P_2O_5 added, p.p.m.	Equivalent Li_2O found, p.p.m.	Error, %
15	79	14·95	− 0·5
15	226	14·8	− 1
15	565	14·75	− 1·5
15	1130	14·35	− 4·5

It will be seen that aluminium has no interfering effect at the relevant levels, and that sulphuric acid has a definite depressing effect on the lithium emission. (It is the sulphuric acid that causes the error in Table V.) Phosphoric acid has a small depressing effect.

In practice these effects are allowed for as shown in Table VIII by the addition of potassium, rubidium, sulphuric acid and phosphoric acid to the lithium standards in amounts depending on the ore being analysed and the method of attack used.

TABLE VIII

ADDITIONS REQUIRED TO LITHIUM STANDARDS

Lawrence Smith attack—

Ore	Sample weight, g	Lithium standard, p.p.m. of Li_2O	KCl required, p.p.m.	RbCl required, p.p.m.
Amblygonite ..	0·5	15	nil	nil
		10	nil	nil
		5	nil	nil
Lepidolite ..	0·5	15	52·5	15
		10	35	10
		5	17·5	5

Berzelius attack—

All standards contain 25 ml of 50 per cent. w/w sulphuric acid per litre

Ore	Sample weight, g	Lithium standard, p.p.m. of Li_2O	P_2O_5 required, p.p.m.	K_2SO_4 required, p.p.m.	Rb_2SO_4 required, p.p.m.
Amblygonite ..	0·15	15	79	nil	nil
		10	53	nil	nil
		5	26	nil	nil
Lepidolite ..	0·3	15	nil	63	16·0
		10	nil	42	10·7
		5	nil	21	5·3

These figures in this Table are based on—

(*a*) amblygonite, 9 per cent. of Li_2O; 47·5 per cent. of P_2O_5;
(*b*) lepidolite, 4 per cent. of Li_2O; 9 per cent. of K_2O; 3 per cent. of Rb_2O.

The interfering substances (with the exception of sulphuric acid) are assumed to vary in proportion to the lithium content.

A comparison of results obtained on the same ore by all three methods investigated is given in Table IX.

Many determinations were conducted on amblygonite C because of the discrepancies between the results of the earlier analyses. The reason for these discrepancies has not been discovered; all that can be said is that the differences confirm the view that the Lawrence Smith ether - ethanol method is not the most reliable for lithium determinations. The Lawrence Smith method followed by flame photometry also suffers from the disadvantage that the attack does not get all the lithium into solution. It is therefore concluded that the Berzelius attack followed by flame photometry is the most accurate (and incidentally the most rapid) method for the determination of the lithium content of ores. A detailed description of this method follows.

TABLE IX

COMPARISON OF RESULTS

All figures are expressed as percentage of Li_2O in the ore

Column A. Accepted values from weight of lithium sulphate.
Column B. Values from lithium content, determined by flame photometer, of lithium sulphate.
Column C. Total known loss in residues, ether - ethanol method.
Column D. Value by flame photometer after Lawrence Smith attack.
Column E. Known loss in residues, flame-photometer method.
Column F. Value by flame photometer after Berzelius attack.

	Lawrence Smith attack							
	Ether - ethanol				Flame photometry			
Ore	A	B	C	Sum of B and C	D	E	Sum of D and E	Berzelius attack F
Lepidolite G ..	3·97	3·87	—	—	—	—	—	4·03
	3·87	3·76	0·10	3·86	3·88	0·03	3·91	3·98
Lepidolite H ..	3·93	3·88	0·06	3·94	3·77	—	—	—
	3·37	3·29	0·65	3·94	3·77	0·07	3·84	3·89
	3·99	3·85	0·08	3·93	—	—	—	3·92
Amblygonite C..	8·61	8·50	0·08	8·58	8·90	—	—	9·25
	8·54	8·69	0·06	8·75	9·10	—	—	9·32
	8·61	8·57	0·09	8·66	9·05	—	—	—
	9·05	—	—	—	9·05	—	—	—
	8·63	8·55	—	—	9·21	—	—	—
	9·00	8·94	0·06	9·00	9·17	0·06	9·23	—
	9·33	9·19	—	—	9·23	0·06	9·29	—
	9·07	8·98	0·06	9·04	9·13	0·05	9·18	—
	9·23	9·11	0·06	9·17	—	—	—	—
Amblygonite D..	8·32	—	—	—	8·67	—	—	—
	8·29	—	—	—	8·62	—	—	8·70
Amblygonite E..	7·75	8·15	—	—	8·11	—	—	—
	7·77	7·67	—	—	8·13	—	—	8·25
	7·67	7·56	—	—	—	—	—	—
Petalite	4·06	—	—	—	4·25	—	—	4·20
	4·08	—	—	—	4·24	—	—	4·16
Spodumene ..	5·65	—	—	—	5·98	—	—	6·04

METHOD

The method is intended for use with the E.E.L. flame photometer, and is not necessarily suitable for instruments of other makes.

REAGENTS—

Sulphuric acid, 50 per cent. w/w, sp.gr. 1·400.

Phosphoric acid, dilute—Dilute 2 ml of phosphoric acid, sp.gr. 1·75, to 1 litre with distilled water.

Potassium sulphate - rubidium sulphate solution—Dissolve 0·167 g of AnalaR potassium sulphate and 0·043 g of rubidium sulphate and make up to 200 ml with distilled water.

Lithium sulphate containing 4000 *p.p.m. of* Li_2O (A)—Weigh out 4·946 g of pure lithium carbonate (dried for ½ hour at 110° C) and wash it into a 300-ml conical flask with a funnel in the neck. Add distilled water to a total volume of 100 to 150 ml. Add slowly through the funnel 27·4 ml of 5 *N* sulphuric acid, and gently boil the solution until all the carbonate has dissolved and the carbon dioxide has been driven off. Cool, transfer to a 500-ml calibrated flask, add 25 ml of mercuric chloride solution (10 p.p.m.) and make up to the mark with distilled water.

Lithium sulphate containing 200 *p.p.m. of* Li_2O (B)—By pipette put 25 ml of lithium sulphate solution *A* into a 500-ml calibrated flask, add 25 ml of mercuric chloride solution (10 p.p.m.) and make up to the mark with distilled water.

Working standard containing 15 *p.p.m. of* Li_2O—(*a*) For lepidolite analysis: take 15 ml of lithium sulphate solution *B*, 15 ml of potassium sulphate - rubidium sulphate solution and 5 ml of 50 per cent. w/w sulphuric acid and make up to 200 ml with distilled water.

(*b*) For amblygonite analysis: take 15 ml of lithium sulphate solution *B*, 7 ml of dilute phosphoric acid solution and 5 ml of 50 per cent. w/w sulphuric acid and make up to 200 ml with distilled water.

Working standard containing 10 *p.p.m. of* Li_2O—(*a*) For lepidolite analysis: take 10 ml of lithium sulphate solution *B*, 10 ml of potassium sulphate - rubidium sulphate solution and 5 ml of 50 per cent. sulphuric acid and make up to 200 ml with distilled water.

(*b*) For amblygonite analysis: take 10 ml of lithium sulphate solution *B*, 4·7 ml of dilute phosphoric acid solution and 5 ml of 50 per cent. w/w sulphuric acid and make up to 200 ml with distilled water.

Certain of the standard solutions are made up to contain about 0·5 p.p.m. of mercuric chloride in order to prevent the growth of moulds, which interfere with the smooth performance of the atomiser.

PROCEDURE FOR SOLUTION OF THE ORE—

The approximate weight of ore required is 0·15 g if the Li_2O content is 8 to 9 per cent. and 0·3 g if the Li_2O content is about 4 per cent.

Grind rather more than the required amount of ore in an agate mortar until no gritty pieces are perceptible. Weigh out the required quantity of this ground sample in a platinum dish. Add about 10 ml of 40 per cent. AnalaR hydrofluoric acid and 5 ml of concentrated nitric acid and evaporate to dryness on a water bath in a fume-chamber. Add about 5 ml of distilled water and evaporate to dryness. Repeat the treatment with hydrofluoric and nitric acids and again evaporate to dryness.

Add about 5 ml of distilled water and 10 ml of 50 per cent. sulphuric acid, and evaporate as far as possible on the water bath. Transfer the dish to a hot-plate, or heat over a small flame to drive off the sulphuric acid to dryness. The heating should not be sufficient to cause loss by spitting or by creeping of the contents over the edge of the dish.

Add about 10 ml of water and 25 ml of 50 per cent. w/w sulphuric acid, and heat on the water bath (with addition of distilled water if necessary) until the solid is detached from the platinum dish. Wash out completely into a 600-ml beaker, add water to bring the volume to about 400 ml and bring to the boil. Cover the beaker with a clock-glass and allow to digest on the hot-plate until solution is complete. A small insoluble residue sometimes remains when a sample of lepidolite is examined.

Cool, filter into a 1-litre calibrated flask, make up to the mark with distilled water and use this solution for analysis by flame photometry.

PROCEDURE FOR FLAME PHOTOMETRY—

Light the flame and adjust the instrument according to the makers' instructions. Spray the appropriate 15 p.p.m. working standard solution into the flame and adjust the sensitivity control to give a reading of about 60 on the linear scale. Spray distilled water into the flame for at least 1 minute and adjust the zero.

Without re-adjusting the sensitivity, take readings in succession of the 15 p.p.m. standard, the unknown solution and the 10 p.p.m. standard. Continue to take readings of the three solutions in the same order, without adjusting the sensitivity, until six sets of values have been obtained, which should be free from any pronounced drift from one series to the next.

If A is the reading of the 15 p.p.m. standard,
B is the reading of the 10 p.p.m. standard,
C is the reading of the unknown solution, and
Y is the p.p.m. of Li_2O in the unknown solution—

$$Y = \frac{C - B}{A - B} \times 5 + 10.$$

The average ($\bar{Y}$) of the six values for Y is then taken.

The lithium content of the ore is given by—

$$Li_2O, \text{ per cent.} = \frac{\bar{Y}}{10 \times \text{weight of ore taken}}.$$

PROCEDURE FOR ORES OTHER THAN LEPIDOLITE AND AMBLYGONITE—

For the most accurate results, these ores may require special standards. For the analysis of spodumene or petalite, standards containing 10 and 15 p.p.m. of Li_2O with 5 ml of 50 per cent. w/w sulphuric acid per 200 ml of solution are suitable.

I thank Messrs. Alfred H. Knight for a description of their method of attack on lithium ores, Mr. J. Hogan and Mr. R. F. Trew, who have carried out some of the analyses referred to, and Mr. L. M. Miall for his assistance in the preparation of this paper for publication. The work was carried out in the laboratories of Kemball, Bishop & Co. Ltd., to whose directors I am grateful for permission to publish these results.

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The Determination of Aluminium in Iron and Steel with the Aid of Chromatographic Separation

BY J. R. BISHOP

The separation of aluminium from steel on a cellulose column is described, and it is shown that large amounts of iron can be removed from a cellulose column while aluminium is quantitatively retained. The aluminium is then removed by eluting with dilute acid and is subsequently determined polarographically.

The method is rapid, is capable of routine operation and requires only simple apparatus. The results obtained on a variety of steels are given.

THE determination of aluminium in steel is difficult, the main problem being to separate small amounts of aluminium from large amounts of iron. Separations described in the literature, including precipitation of aluminium as hydroxide under controlled conditions, mercury-cathode electrolysis, cupferron precipitation and extraction of iron by organic solvents, are usually tedious and incomplete. A method of mercury-cathode electrolysis recently published,[1] in which a new type of cell is used, achieves separation in a single stage and is not too time-consuming, but the cleaning and storage of relatively large amounts of mercury, when many determinations are carried out, can be a problem.

In recent years metal separations by chromatography of inorganic ions have become available, and are often quicker and easier than the classical procedures. Work carried out in these laboratories[2] has shown that small quantities of aluminium can be separated easily when in solution together with nickel, manganese, lead, cobalt, bismuth, copper, zinc and iron; this method was used for the determination of aluminium in tin - lead solders, after the bulk of the main metals had been removed by a preliminary treatment. Subsequent experience showed that it was possible to remove large quantities of iron from a cellulose column while aluminium was retained; no preliminary separation was needed. A similar

separation, cobalt and nickel being isolated from steel, had been indicated already by Burstall, Davies and Wells,[3] but this procedure seems to have been little used in steel analysis.

The procedure arrived at after preliminary experiments is essentially simple. A concentrated solution of the steel to be analysed is applied to the top of a short cellulose column. The iron and the bulk of most of the alloying metals are removed by elution with acidified ethyl methyl ketone, and aluminium and nickel are left in the top portion of the column. The metals are then recoverable by elution with dilute acid, and the aluminium can be determined in the resulting solution after suitable concentration.

The method of Willard and Dean,[4] which gives a polarographic wave by the reduction of the complex formed between aluminium and an azo dye, has been found very convenient. For mild steels it could be applied directly to the eluate after evaporation and simple treatment. Large amounts of nickel interfere, however, and must be removed.

Method for plain steels

Preparation of sample for chromatography—

Weigh 0·1 to 1·0 g of steel, choosing the weight so that the amount of aluminium will be about 50 μg. Place the sample in a 250-ml tall beaker, and dissolve it with gentle heating in 10 ml of concentrated hydrochloric acid. Add 10 ml of water and oxidise by dropwise addition of 1 ml of 100-volume hydrogen peroxide. Simmer until excess of peroxide is removed and then evaporate to about 5 ml. Allow to cool and add quickly, *i.e.*, not by gradual addition, a suitable amount of freshly distilled ethyl methyl ketone, followed if necessary by drops of concentrated hydrochloric acid, in order to form a homogeneous solution. The details of this step vary according to the type of steel being analysed: certain alloy steels tend to give solutions having two phases, and this must be avoided; for a simple mild steel, however, no difficulty is found if the amount of ketone is 25 to 50 ml. Transfer this solution to a prepared cellulose column.

Preparation of cellulose column—

Prepare the column with aqueous acid to remove any contaminating aluminium. Add 5 g of cellulose powder (Whatman, Standard grade) to 90 ml of diluted hydrochloric acid (1 + 5) and pour this slurry into a silicone-treated chromatographic tube. Allow the column to settle and then to drain; wash it successively with 200 ml of diluted hydrochloric acid (1 + 5), 200 ml of water, 100 ml of freshly distilled ethyl methyl ketone and 100 ml of an eluent prepared by mixing 80 ml of constant-boiling hydrochloric acid with 1920 ml of freshly distilled ethyl methyl ketone.

Separation of aluminium—

Transfer the sample solution to the column with small washings of the ketone eluent, allowing the column to drain between washings. Wash the column with about 2-ml portions of the ketone eluent, rinsing the walls above the cellulose with each addition, until all iron is washed away from the column. Add 50 ml more of eluent and allow to drain. Reject the eluate. Recover the aluminium, which remains at the top of the cellulose column together with any nickel, by passing 200 ml of diluted hydrochloric acid (1+5) through the column.

Determination of aluminium—

Evaporate the solution obtained as described above to dryness, add 0·5 ml of 60 per cent. perchloric acid, cover the beaker and heat to fuming, uncover and evaporate to dryness. Dissolve the residue in a few drops of diluted perchloric acid (1+1), add 2 drops of methyl red solution and carefully make the solution just alkaline with 10 per cent. sodium hydroxide. Re-acidify by dropwise addition of *N* perchloric acid and then add 0·2 ml of 5 *N* perchloric acid. Add 1 ml of 2 *N* sodium acetate solution and 5 ml of a 0·1 per cent. solution of Solochrome violet RS, transfer to a 10-ml calibrated flask and dilute to the mark. Immerse the flask for 5 minutes in a water bath at 55° to 70° C, allow it to cool, de-aerate the solution, and record a polarogram between 0 and — 0·8 volt against a standard calomel electrode, using a dropping-mercury cathode.

Note on method—

With steels containing small amounts of aluminium it is necessary to observe all the precautions used in trace-metal analysis. The materials used in large quantities, hydrochloric

acid and ethyl methyl ketone, are best purified by redistillation. With reasonable care the blank readings can be kept below or near to the limits of detection.

For routine analysis of steels containing moderate amounts of aluminium the columns can be prepared from cellulose and ketone eluent without the acid wash, provided adequate blank columns are used.

Modification for steels containing nickel in alloying amounts

In the chromatographic separation, nickel remains on the column, together with aluminium, after elution; it likewise accompanies the aluminium in the acid solution washed off the column. The amount of nickel in plain steels is insufficient to interfere with the polarographic aluminium determination, but alloying amounts give concentrations that interfere significantly. Nickel can be removed from such steels to an extent sufficient to render the polarographic determination of aluminium possible, by a short small-scale mercury-cathode electrolysis, in a simple cell, carried out on the solution obtained from the column. The need for such a separation would of course not exist if the aluminium were to be determined by a method with which nickel would not interfere.

Results

To test the method for plain steels, known amounts of aluminium were added to known weights of aluminium-free steel, which were then taken through the described procedure. The recoveries are shown in Table I.

Table I

Recovery of added aluminium from 0·5-g portions of an aluminium-free plain steel

Aluminium added, μg	Aluminium recovered, μg	Recovery, %
600	576	96
400	376	94
300	288	96
200	200	100
30·0	29·0	97
22·5	24·5	109
20·0	21·0	105
15·0	14·5	97
10·0	8·5	85
5·0	5·5	110
5·0	4·5	90

Table II

Typical results for various steels

Steel	Aluminium content reported by other workers, %	Aluminium found by present method, %
MGS/182*	0·004 to 0·005	0·003 0·004
MGS/183*	0·016 to 0·019	0·025 0·020 0·020 0·019
L.K. Nitriding steel ..	1·25	1·28 1·27 1·18 1·26
B.C.S. 255	~0·05	0·049 0·049 0·043 0·044

* Analysed by Methods of Analysis Committee of the Metallurgy Division of the British Iron and Steel Research Association.[5]

A large number of aluminium determinations on un-alloyed steels have been carried out successfully by this method over the last few years in these laboratories.

Determinations were carried out on several steels already analysed and reported by other workers. The results are shown in Table II. Most of these analyses included the mercury-cathode electrolysis for nickel removal.

Conclusions

The figures given in Tables I and II confirm that large quantities of iron can be removed on a cellulose column while aluminium is retained quantitatively. The main advantages of the method are rapidity, simplicity of apparatus and the clear-cut separation obtained. Even when the additional step of a small-scale mercury-cathode electrolysis is necessary in order to remove nickel, the method is still rapid and capable of routine operation; the small amount of mercury used in the separation is only slightly contaminated with nickel and is easily removed.

Thanks are due to Dr. H. Liebmann for constant encouragement during the investigation, to Mr. B. T. G. Layzell, who carried out some of the comparative work, and to Mr. J. O. Lay of the British Iron and Steel Research Association, who supplied the analysed steels.

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Micro-determination of Mercury in Biological Materials

By F. R. BARRETT

The difficulties associated with the determination of traces of mercury in materials with a high content of organic matter are discussed and the need for complete oxidation is stressed. Certain modifications of the Cholak and Hubbard digestion procedure and of the Laug and Nelson complexing technique are suggested. The complete method is described and experimental results indicating the reproducibility and accuracy, together with mercury levels in the blood of a few exposed individuals, are recorded.

Digestion

Special digestion procedures are required to determine traces of mercury in the presence of much organic matter because of its relatively high volatility and that of its compounds. The difficulties are increased when it is necessary to use a relatively large sample of animal tissue, *e.g.*, blood, in order to obtain sufficient mercury for determination.

Laug and Nelson[1] used a (1 + 1) mixture of concentrated sulphuric and nitric acids, boiling the sample with it under reflux. A one-tenth aliquot part of the digest was taken to avoid excessive oxidation of the extracting reagent, which markedly reduces the sensitivity of the method.

Cholak and Hubbard[2] were able to use the whole of the digest by treating it with potassium permanganate, after removing fatty material by filtration. The rationale of the procedure appears to be as follows: the oxides of nitrogen formed during nitration reduce the permanganate and re-formed nitric acid is evolved from the concentrated digest. This additional treatment also destroys more of the organic matter.

In agreement with Simonsen,[3] it has been found that, in the absence of a protein-carrier, there is loss of mercury if much nitric acid is allowed to escape from a boiling digest through the top of the condenser. The manner and degree of heating, therefore, is important at this

stage. It has been found that the oxidation - reduction reaction can be effected, without loss of mercury, by moderate heating. Under such conditions, the destruction of organic matter is incomplete. The complete destruction of organic matter is necessary to avoid interference by organo-mercury complexes during extraction. In this regard, mercury is unique among metals in its power of forming compounds with organic radicals.[4] (These organic complexes are decomposed in boiling concentrated acids,[4] but the possibility of re-formation on dilution before extraction cannot be ignored.) A second treatment with permanganate, after suitable dilution of the digest, therefore, has been introduced. This additional treatment also serves to oxidise fatty material that may have escaped through the filter.

Since the proposed digestion procedure is slow and tedious when large samples are taken, it has been customary to limit the size of the sample to a suspected mercury content of, say, 10 to 20 μg or less. Sometimes it may be necessary to reduce the tissue or organ to a fine state of subdivision by grinding in order to obtain a representative sample. With blood, for example, 20 g are usually required, because of the low concentration of mercury encountered. Practical difficulties preclude the use of larger samples. However, in view of the blood figures obtained in exposed persons (Table IV, p. 298) and the sensitivity of the method (0·5 μg of mercury can be detected in 20 g of blood) the above amount is sufficient for a micro method.

Extraction

Interference from manganese, hydroxylamine, chloride ions, copper and other heavy metals, reported by other workers, has been further studied by the author.[5] The digest solutions are diluted, in accordance with my findings, to permit complete extraction of mercury by dithizone in chloroform within reasonable shaking times and to prevent subsequent interference from copper.

I have developed[5] a direct extraction technique for mercury in urine, based on my finding that the minute amounts of copper present are not co-extracted under the conditions used.

However, there is sufficient copper in many biological materials to interfere, particularly when only minute traces of mercury are present. Moreover, a far greater source of error is possible when nitric acid is used for digestion. Fischer[6] states that dithizone is oxidised, under weak oxidising conditions, to diphenylthiocarbodiazone. This product is soluble in chloroform to give yellow solutions similar in colour to the yellow - orange solutions of mercury dithizonate. The oxidation is not always prevented by the addition of hydroxylamine. Anyway, too great an excess of this reagent should be avoided. A preliminary extraction of the metal, therefore, is considered necessary.

The two complexing agents available for an initial extraction are Winkler's acid thiosulphate[7] and Laug and Nelson's acid bromide. Low results were obtained with Winkler's method and also with Cholak and Hubbard's modification, even when no sulphur was visible, being present probably in the colloidal or "soluble" form. Simonsen also reported difficulty with this reagent. The instability of thiosulphuric acid, with formation of sulphur and consequent loss of mercury-complexing ability and the difficulty of deciding whether the sulphur had been completely oxidised by subsequent treatment, led me to investigate further the Laug and Nelson reagent.

Laug and Nelson's acid bromide procedure was tried previously for urine digests, but low recoveries (80 to 95 per cent., according to the amount of mercury present) were obtained. Wichmann[8] and Arthington and Hulme[9] also reported difficulty with this method.

The influence of hydrogen-ion and halide-ion concentration and time of shaking upon the extractability of mercury and copper was studied by Irving, Andrew and Risdon.[10] Their findings have been used as a basis for further experimental work and excellent results have been obtained with the following modifications of the acid bromide procedure—

(1) Substitution of sulphuric acid for hydrochloric acid. There is a definite disadvantage in using the latter reagent, particularly when the whole of the digest is taken for extraction, because of the resultant high acidity. Irving and his co-workers showed the advantage of using sulphuric acid as free from chloride ions as possible. Partial neutralisation with redistilled ammonia before extracting, as suggested by Laug and Nelson, becomes no longer necessary. Prolonged shaking is not recommended because of increased co-extraction of copper and subsequent partial reversion by hydrogen ions,

particularly when large amounts of copper are present in the original material. The use of 0·25 *N* hydrochloric acid, therefore, has been eliminated from the whole procedure.

(2) Limiting the amount of mercury for complexing to 8 μg and increasing the amount of bromide, in accordance with the following experimental results—

Amount of mercury present, μg		1	4	8	10
Mercury extracted with 50 ml of 0·25 *N* H_2SO_4 containing	(*i*) 5 ml of 40% KBr solution, % ..	100	97·5	94	92
	(*ii*) 10 ml of 40% KBr solution, % ..	—	—	100	98·5
	(*iii*) 2 × 5 ml of 40% KBr solution, % ..	—	—	—	100

Dithizone extracts, containing various amounts of mercury as dithizonate, were shaken with sulphuric acid - potassium bromide solutions as indicated above. The aqueous phase, containing mercury as K_2HgBr_4, was then brought to pH 6 to destroy the complex and the mercury was extracted with dithizone solution (6 mg in 1 litre of chloroform).

As indicated above, larger amounts of mercury may be taken by repeating the bromide treatment, that is, shaking the extract with 5 ml of bromide in 25 ml of acid solution, transferring the extract to another separating funnel, repeating the acid bromide treatment, discarding the extract and combining the aqueous layers. However, in view of the accuracy of the simpler procedure, see Table I, the repetitive acid bromide treatment is considered unnecessary.

(3) Protecting the mercury dithizonate against light. Laug and Nelson state that determinations should be carried out in artificial or subdued light and cite Winkler that the intense light of certain optical instruments has the same but less pronounced effect. To overcome this disadvantage of photosensitivity, Cholak and Hubbard used an analogue of dithizone, di-2-naphthylthiocarbazone, as the colorimetric reagent. However, this reagent is difficult to purify. Dithizone has been retained and the following precautions have been taken: (*a*) housing the separating funnels in a dark cabinet, situated at bench level for convenience; the cabinet also serves to protect the separating funnels from dust; and (*b*) using an E.E.L. colorimeter (Evans Electroselenium Ltd.), whose source of light is a 2-volt lamp that may be fed from a large 2-volt battery.

The precision and accuracy of the modified Laug and Nelson extraction procedure were tested as follows—

Some 100-ml solutions of 1·4 *N* sulphuric acid containing 1 ml of 50 per cent. hydroxylamine hydrochloride and differing amounts of mercury were carried through the modified procedure.

Six replicates were tested at each mercury level. The results, after subtraction of the reagent blank, are shown in Table I.

TABLE I

PRECISION AND ACCURACY OF THE EXTRACTION PROCEDURE

Mercury added, μg	Mercury found: Highest result, μg	Mercury found: Lowest result, μg	Mean	Fiducial limits (P = 0·95)
1·00	1·05	0·95	1·02	0·984 to 1·056
4·00	4·05	3·95	4·00	3·964 to 4·036
8·00	8·00	7·95	7·98	7·951 to 8·009

METHOD

REAGENTS—

Sulphuric - nitric acid mixture—Equal volumes of the concentrated acids.

Sulphuric acid, 0·25 *N*—Prepared from glass-distilled water.

Hydroxylamine hydrochloride—A 50 per cent. w/v solution (purified).

Potassium bromide—A 40 per cent. w/v solution (purified).

Buffer solution—150 g of disodium hydrogen phosphate and 38 g of anhydrous potassium carbonate in 1 litre of solution (purified).

Dithizone solution—6 mg of dithizone per litre of redistilled chloroform (purified). Each 10-ml portion of reagent extracts approximately 15 μg of mercury.

Standard mercury solution, 0·100 per cent.—Prepare as described by Sandell.[11]

Potassium permanganate—0·5-g tablets.
Purify the reagents as described by Sandell.[11]

PROCEDURE FOR PREPARING SAMPLE—

The following quantities are recommended:
(*a*) 1 to 4 g of tissue + 8 ml of acid mixture;
(*b*) 4 to 10 g of tissue + 20 ml of acid mixture;
(*c*) 10 to 20 g of tissue + 30 ml of acid mixture.

Transfer the solid tissue or blood to a dry 500-ml digestion flask fitted with a cold-finger condenser.[5] Add sulphuric - nitric acid mixture and a few Pyrex-glass chips for smooth boiling. Heat the flask gently over a micro gas burner until foaming ceases, then raise the temperature gradually to avoid spluttering, and boil gently for 2 hours. Cool the solution, finally in an ice-bath, and remove fatty material by filtering through a tight plug of glass-wool in a filter-funnel. Collect the clear filtrate in a 1-litre digestion flask, rinse with 4 ml of diluted sulphuric acid (1 + 3) and run the washings through the funnel into the flask. Re-insert the condenser and add a tablet (0·5 g) of potassium permanganate. Heat the flask slowly over a small flame until the solution is decolorised. Allow to cool for a few minutes and repeat the procedure, adding one tablet at a time, until 5 or 6 tablets per 10 g of sample have been added and a precipitate of manganese dioxide persists after boiling. Do not boil until acid fumes have subsided (see p. 294).

Without removing the condenser, add 50 ml to 100 ml of water to the flask (depending on the amount of acid used). Complete the digestion by adding permanganate tablets, one at a time, to the gently boiling digest until the permanganate colour persists and any fatty material present has been oxidised.

Cool the solution and decolorise it with 50 per cent. hydroxylamine hydrochloride. The digest should be colourless or show only the faintest tinge of yellow. Dilute to (*a*) 150 ml, (*b*) 300 ml or (*c*) 400 ml, according to the amount of acid used (*vide supra*), and proceed with the extraction without undue delay and in subdued light, preferably with the separating funnels housed in a dark cabinet.

With blood samples, transfer the whole of the digest to a separating funnel, dilute to volume and add 50 per cent. hydroxylamine hydrochloride (1 ml per 100 ml of solution). For duplicate analysis, take another blood sample.

With solid tissue, dilute to volume, take one-half aliquot, add the requisite amount of hydroxylamine and 5 ml of dithizone solution and shake. Continue the extraction, if necessary, to find the range. Select an aliquot containing less than 8 μg of mercury, make up to a suitable volume with 1·4 *N* sulphuric acid and add the requisite amount of hydroxylamine. For duplicate analysis, use digest solution.

For urine samples, the method previously described is recommended because of its simplicity, combined with accuracy. If greater sensitivity is required, take 50 ml of urine and use the whole of the diluted digest for extraction by the procedure described in this paper.

PROCEDURE FOR INITIAL EXTRACTION—

Shake the solution, or dilute standard, in the first separating funnel with 10 ml of dithizone reagent for 1 minute. After the mixture has layered, transfer the extract to a second separating funnel containing 50 ml of 0·25 *N* sulphuric acid. Repeat the extraction in the first funnel with a further 10 ml of dithizone reagent. Combine the two extracts in the second funnel and wash by shaking for 30 seconds.

Transfer the washed extracts quantitatively to a third funnel containing 50 ml of 0·25 *N* sulphuric acid. Add 10 ml of 40 per cent. potassium bromide and shake vigorously for 45 seconds. Discard the chloroform layer and wash the aqueous phase (containing mercury as K_2HgBr_4) by shaking with 10 ml of chloroform. Remove the chloroform as completely as possible.

PROCEDURE FOR FINAL EXTRACTION—

Treat the aqueous phase with 10 to 11 ml of the buffer solution to raise the pH to about 6 (test with pH paper). Add exactly 10 ml of dithizone reagent and shake for 1 minute. Run the chloroform extract through a plug of absorbent cotton-wool inserted in the shortened

stem of a separating funnel, discarding the first ½ ml. Collect the clear filtrate in a suitable tube and measure the absorption at 490 mμ.

A blank must be carried through the whole procedure.

Results

The reproducibility and accuracy of the extraction technique are shown in Table I. The reliability of the method for recovering mercury from animal tissues was determined by adding various amounts of mercuric chloride to liver and blood samples and carrying out the digestion and extraction as described above. The results are given in Tables II and III.

The figures given in Table IV demonstrate, in agreement with Cholak and Hubbard, the need for a micro method capable of dealing with relatively large samples of blood. The blood and urine samples were obtained from three exposed persons working in the same laboratory. The blood figures are relatively higher than those record d by Cholak and Hubbard.

Table II

Recoveries of mercury added to blood samples

Blood sample, g	Number of tablets of potassium permanganate used	Mercury added, μg	Mercury found, μg
20	20	0	0·9, 1·0
20	20	0·5	1·4, 1·4
20	20	2·0	2·7, 3·0
10	10	0	0·6, 0·7
10	10	5·0	5·4, 5·6
10	10	10·0	10·6, 11·0

Table III

Recoveries of mercury added to liver samples

	Liver used, g	Number of tablets of potassium permanganate used	Mercury added, μg	Mercury found, μg
No. 1	20	20	0	2·1
	20	20	5·0	7·5, 6·9
No. 2	10	10	0	0·9, 1·0
	10	10	10·0	10·6, 10·8

Table IV

Concentration of mercury in blood and urine of exposed persons

Name	Mercury found in urine (24-hour excretion), mg	Blood sample, taken, g	Mercury found in blood, mg per 100 g
W.G.	0·30	21·5, 21·2	0·002, 0·002
P.D.	0·18	23·7, 19·5	0·003, 0·003
D.W.	0·19	25·7, 24·0	0·003, 0·003

The author thanks the Director-General of Health, Canberra, for permission to publish this paper.

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The Colorimetric Determination of Chloramphenicol

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Details of a colorimetric method for the determination of chloramphenicol are given. The method utilises the production of a red colour resulting from the interaction of the nitro group of chloramphenicol with a dimethylformamide - acetone solution in the presence of tetraethylammonium hydroxide.

THE antibiotic chloramphenicol has been determined by the reduction of the aryl nitro group to an amine with titanous chloride,[1] stannous chloride[2] or zinc dust.[3] The amine produced by these methods has then been diazotised and coupled with N-(1-naphyl)ethylenediamine dihydrochloride[4] or 2-naphthol.[5] Another method involves hydrolysis of chloramphenicol with acid and then oxidation with iodate to *p*-nitrobenzaldehyde, which was determined by means of 2:4-dinitrophenylhydrazine.[6] Picric acid[7] has also been used to produce a reddish-brown colour with chloramphenicol. In this paper a direct colorimetric determination based on the production of a stable red colour with the aryl nitro group of chloramphenicol is described.

Certain previous colorimetric methods for the determination of mononitro compounds have relied on the conversion to the corresponding dinitro compound, which could then be determined by the production of a red-violet colour with acetone and alkali. Substituted mononitro compounds have been determined by means of the yellow colour produced in aqueous alkali, and it has been reported that 4-amino-3-nitrotoluene gives an orange colour with acetone and alkali.[8]

In a recent investigation[9] into the determination of atropine by nitration and subsequent production of a colour with acetone and alkali, the author succeeded in stabilising the colour produced from the dinitro compound formed on nitration by the substitution of dimethylformamide and tetraethylammonium hydroxide for the more usual reagents, acetone and alkali.

After the success with this dinitro compound, an attempt was made to apply these reagents to the determination of certain mononitro compounds. It was, however, observed that with substituted mononitro compounds, such as *p*-nitroaniline, yellow colours were produced under all conditions and that with others, such as chloramphenicol, yellow colours were produced at low concentrations and orange-yellow to red at higher concentrations after standing for some time. Nitrobenzene on standing gave a red colour on addition of tetraethylammonium hydroxide to a solution in dimethylformamide. These observations with the exception of those on nitrobenzene seemed to agree with the findings of others, namely, that only in special conditions were colours other than yellow produced with mononitro compounds on the addition of solvent and base.

With chloramphenicol the colour produced with tetraethylammonium hydroxide and dimethylformamide did not obey Beer's law over the range investigated, but it gave an upward inflexion at higher concentrations on a graph of colour against concentration. This deviation seemed to indicate that more than one reaction was taking place and, although the experimental conditions were varied considerably, a linear plot was not obtained. One other fact observed, however, was that on the addition of tetraethylammonium hydroxide to a hot solution of dimethylformamide and nitro compound, the formation of a green colour, changing slowly through green-blue to red, occurred. Green colours have not hitherto been reported in the reaction of nitro compounds with solvent and base, although common with nitroso compounds, and it might be interesting to speculate on the course of the reaction involved.

After some experiments with different solvents, it was found that by the use of dimethylformamide containing very small amounts of acetone, or sometimes methyl cyanide, red colours suitable for quantitative determinations could be obtained from mononitro compounds in the presence of base.

The amount of acetone employed in the dimethylformamide solution is not critical, but if excess were present, it would react with dimethylformamide in the presence of base to give a yellow colour, interfering with the subsequent determination of the nitro compound. The use of acetone in dimethylformamide, as well as giving a colour that followed Beer's

law, gave an increase in the intensity of colour produced when compared with the colour eventually produced in the absence of acetone, on the addition of tetraethylammonium hydroxide to a solution of chloramphenicol in dimethylformamide.

Experimental

Fig. 1 illustrates the change in absorption spectra resulting from the use of a dimethylformamide - acetone solution in the place of dimethylformamide in the production of colour from chloramphenicol in the presence of base.

Effect on colour intensity of a variation in acetone concentration—

This is illustrated in Fig. 2 and showed that it would be possible to determine acetone in small amounts by a variation of the described method, provided that the concentration of nitro compound was kept constant and a blank correction applied.

Effect of variation in the amounts of tetraethylammonium hydroxide used—

The optimum amount was found to be 0·1 ml of 25 per cent. aqueous solution in a reaction volume of 10 ml. The use of quantities greater than 0·1 ml delayed to some extent the production of the full intensity of the colour.

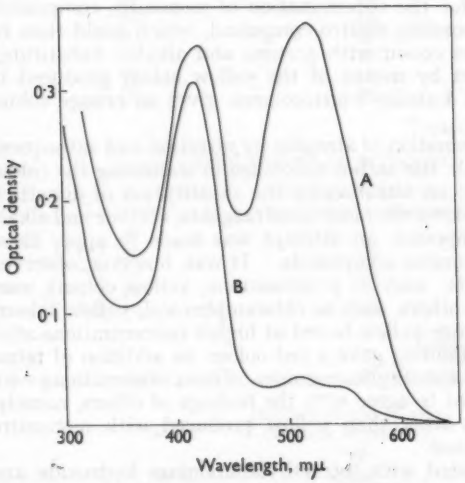

Fig. 1. Absorption spectra of colour produced from chloramphenicol in the presence of base: curve A, in dimethylformamide - acetone solution; curve B, in dimethylformamide solution

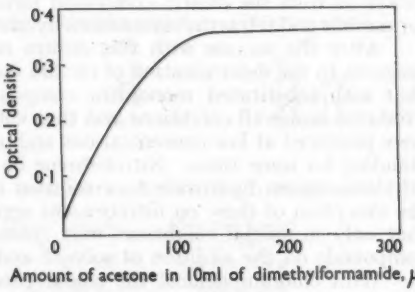

Fig. 2. Effect of acetone concentration on colour intensity

Effect of a variation in the order of the addition of reagents—

It was found that colour was produced more rapidly by adding a solution of chloramphenicol in dimethylformamide to the dimethylformamide, acetone and tetraethylammonium hydroxide mixture rather than by adding tetraethylammonium hydroxide to a solution of chloramphenicol in dimethylformamide and acetone.

Colour development and stability—

It was found that the colour produced by the methods described reached a maximum after approximately 10 minutes and then faded very slowly over a period of hours.

Calibration graph—

Over the range investigated the graph proved to be linear.

Method

Apparatus—

Unicam SP500 spectrophotometer or similar instrument capable of measurement in the visible region; 1-cm cells.

Reagents—

Dimethylformamide—Laboratory-reagent grade (as supplied by The British Drug Houses Ltd.).

Tetraethylammonium hydroxide—A 25 per cent. aqueous solution; laboratory-reagent grade (as supplied by The British Drug Houses Ltd.).

Acetone in dimethylformamide—A freshly prepared 0·1 per cent. solution of acetone in dimethylformamide.

Acetone—Analytical-reagent grade.

Chloramphenicol, B.P.

Procedure—

To 10 ml of dimethylformamide in a clean dry test tube, add 0·2 ml of 0·1 per cent. solution of acetone in dimethylformamide and then add 0·1 ml of 25 per cent. aqueous tetraethylammonium hydroxide. Shake the tube gently to mix the contents. By pipette add to this mixture an aliquot of a solution of chloramphenicol in dimethylformamide containing approximately 0·1 to 0·15 mg of chloramphenicol. Shake the tube gently and then set it aside for 10 minutes.

Measure the colour produced at 520 mμ, using a 1-cm cell and a reagent blank.

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October 24th, 1955

A Direct Micro-alkalimetric Titration Method for Determining Sulphur in Organic Compounds

By J. SMITH and A. C. SYME

A direct micro-alkalimetric titration method for determining sulphur in organic compounds containing nitrogen and chlorine is described. The method is applicable both to wet and dry-combustion methods, the ultimate product, barium sulphate, being treated with an ion-exchange resin, and the liberated acid titrated.

Sulphur in organic substances is generally determined by conversion to sulphuric acid or sulphate, which is then measured gravimetrically or, preferably, volumetrically. Hitherto the direct alkalimetric method has been limited to compounds that do not contain nitrogen or halogen.

The methods of combustion employed are dry[1,2,3] or wet,[4,5,6,7,8] and the sulphur is ultimately determined gravimetrically as barium sulphate. This involves special filtration procedures[1,8,9] and transference of the barium sulphate to a weighed crucible[1,9] fitted with a compressed iridio-platinum or other porous filtering base.

Direct titration of the sulphuric acid formed during combustion in oxygen is impossible, mainly owing to traces of oxides of nitrogen, but indirect titration methods have been investigated.[10,11] Burger[12] reports a successful titrimetric method by converting the sulphur to sulphide by fusion with metallic sodium, and titrating iodimetrically as hydrogen sulphide. In our experience loss of hydrogen sulphide always results.

Yoshino[13] treats the barium sulphate with a mixture of (Na) cation and (Cl) anion-exchange resins. Chloride is liberated and is titrated directly, after filtration, with silver nitrate.

The present investigation, based on an observation by Osborn[14] that barium sulphate reacts quantitatively with strongly acid ion-exchange resins, was undertaken to ascertain if a direct alkalimetric-titration method for determining sulphur in organic compounds containing nitrogen and halogen could be developed. The results obtained (Table II, p. 303) show that this is possible.

To determine the best conditions for reaction between barium sulphate and the particular ion-exchange resin, in this instance Amberlite IR-120(H), and also the best conditions for titration, known quantities of barium sulphate, obtained by reaction between sulphuric acid and barium chloride, were treated with the resin. The liberated sulphuric acid was then titrated with carbonate-free 0·01 *N* sodium hydroxide. Results are given in Table I, and the best conditions of titration are described under "Method." The effect of temperature on the rate of dissociation of the barium sulphate is shown in Fig. 1. The most suitable temperature was about 70° C, since at higher temperatures the resin disintegrated, especially if agitated or stirred too vigorously.

Table I

Results by titration method

Volume of 0·01 *N* sulphuric acid, ml	Barium sulphate taken, mg	Volume of 0·01 *N* sodium hydroxide, ml	Barium sulphate recovered, mg
3·71	4·35	3·63	4·26
3·71	4·35	3·65	4·27
3·71	4·35	3·61	4·23

Method

Preparation of resin—

Mix the resin (Amberlite IR-120(H), analytical grade) with approximately twice its volume of 5 per cent. hydrochloric acid (M.A.R.) and stir gently for several hours. Collect the resin on a sintered-glass filter, and wash it thoroughly with distilled water until the filtrate is neutral (approximately 1 litre of distilled water is required). Add the resin to five

Vol. 81, 1956: May, p. 303.

Replace the body of Table II by—

Sulphanilic acid, $C_6H_7O_3NS$	4·558	5·39	18·9	18·5
Thiourea, CH_4N_2S	4·300	11·20	41·7	42·1
Thiosemicarbazide hydrochloride, CH_6N_3ClS	4·231	6·74	25·5	25·1
7 : 8-Dimethoxy-1-oxo-1 : 2-dihydro-2-thianaphthalene-3-carboxylic acid, $C_{13}H_{10}O_5S$	2·945	2·20	12·0	12·0
Methyl ester of above acid, $C_{13}H_{12}O_5S$	4·921	3·49	11·4	11·4
4-Methyl-1-nitrothioxanthone, $C_{14}H_9O_3NS$	3·517	2·68	12·2	11·8
Aminophenol sulphonic ester, $C_7H_9O_4NS$	3·126	3·11	16·0	15·8
Toluene-*p*-sulphonchloride, $C_7H_7O_2ClS$	3·046	3·25	17·1	16·8

TABLE II

DETERMINATION OF SULPHUR IN ORGANIC SUBSTANCES

Substance	Weight taken, mg	Volume of 0·01 *N* sodium hydroxide, ml	Sulphur found, %	Sulphur required in theory, %
Sulphanilic acid, $C_6H_7O_3NS$	4·558	5·39	18·5	18·4
Thiourea, CH_4N_2S	4·300	11·20	41·7	41·6
Thiosemicarbazide hydrochloride, CH_6N_3ClS	4·231	6·74	25·5	25·7
7:8-Dimethoxy-1-oxo-2-thionaphthalene-3-carboxylic acid, $C_{12}H_{10}O_5S$	2·945	2·20	12·0	12·0
Methyl ester of above acid, $C_{13}H_{12}O_5S$	4·921	3·49	11·5	11·4
4-Methyl-1-nitrothioxanthone, $C_{14}H_9O_3NS$	3·517	2·68	12·3	12·5
Aminophenol sulphonic ester, $C_7H_9O_4NS$	3·126	3·11	16·0	15·8
Toluene-*p*-sulphonchloride, $C_7H_7O_3ClS$	3·046	3·10	17·1	16·8

times its volume of distilled water and stir gently at 70° C for 1 hour, and then filter. Titrate the filtrate with 0·01 *N* sodium hydroxide to ascertain the amount of acid, using bromcresol green - methyl red mixed indicator. Continue the washing and titration until the filtrate is neutral or gives a constant value. Store the resin in distilled water.

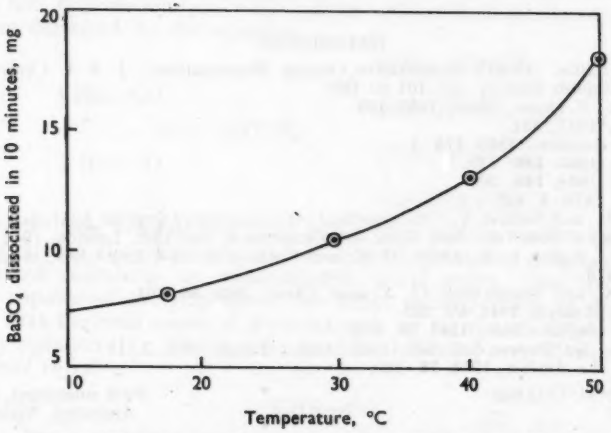

Fig. 1. Effect of temperature on the rate of dissociation of barium sulphate (initial amount 20 mg)

REGENERATION OF RESIN—

After use with barium sulphate, regenerate the resin by the above procedure, but use 10 per cent. hydrochloric acid.

PROCEDURE FOR DETERMINING BARIUM SULPHATE—

Add 0·30 ml of *N* hydrochloric acid to 0·928 ml of 0·01 *N* sulphuric acid in a centrifuge tube. This addition is to render the solution 0·05 *N* when all the sulphate is precipitated, under which conditions the barium sulphate forms comparatively large crystals that are easily centrifuged and washed. Immerse the tube in a boiling-water bath, and add dropwise 2·00 ml of 0·02 *N* barium chloride solution with constant stirring. Continue digestion for 1 hour, and then centrifuge the tube. Remove the supernatant clear liquor by means of a medicine dropper, add distilled water, washing down the medicine dropper, and stir the precipitate either with a thin glass rod or, preferably, a stiff platinum wire. Remove the stirrer, wash down into the tube, and centrifuge. Repeat the washing, stirring and centrifuging until all barium chloride and free acids are removed. Should a small cloud of barium sulphate remain on the surface after centrifuging, the addition of a drop of a wetting agent,

e.g., a very dilute solution of cetylammonium bromide, lowers the surface tension and prevents the cloud forming during subsequent washings.

Transfer the barium sulphate quantitatively to a 250-ml conical flask with a stream of distilled water. Add about 15 g of pretreated resin (Amberlite IR-120(H)) to the flask and make up to 100 ml with distilled water. Immerse the flask in a water bath for 1 hour at about 70°, with brisk but not too vigorous stirring. Filter off by mild suction, through a sintered-glass filter, wash thoroughly with distilled water, and titrate the combined filtrate and washings with 0·01 *N* sodium hydroxide, using bromcresol green - methyl red indicator.

PROCEDURE FOR DETERMINING SULPHUR—

Introduce 3 to 5 mg of sample into a cleaned Carius tube of Pyrex glass, using a long handled weighing stick. Add 10 to 20 mg of barium chloride (M.A.R.) and then 0·3 ml of concentrated nitric acid (M.A.R.); seal the tube and heat it to 280° to 290° C for 1½ hours. After the tube has cooled, release the pressure in the usual way, cut the tube to a length suitable for the centrifuge, and wash down the walls with a jet of distilled water. Unlike the ordinary method, fragments of glass falling into the tube have no effect on the result. Heat the contents on a steam-bath for 1 hour, and treat the barium sulphate as described above. Results on various organic substances are shown in Table II.

The authors thank Professor F. S. Spring and Dr. A. B. Crawford for their interest in the work and Drs. G. T. Newbold and D. C. Munro for some of the specimens containing sulphur.

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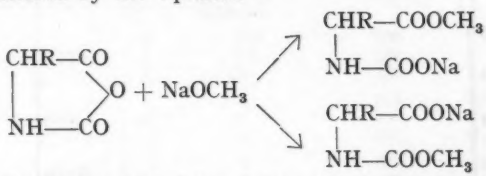
The Titration of N-Carboxy-α-amino-acid Anhydrides in Non-aqueous Solution

By D. G. H. BALLARD, C. H. BAMFORD and F. J. WEYMOUTH

Berger, Sela and Katchalski have described a procedure for the determination of N-carboxy-α-amino-acid anhydrides by titration with sodium methoxide in non-aqueous solution. As recent work in these laboratories showed that sodium methoxide is a powerful catalyst for the polymerisation of many of the anhydrides (a fact apparently not known to Berger *et al.*), it became necessary to re-examine the validity of the method of determination and the nature of the reactions occurring.

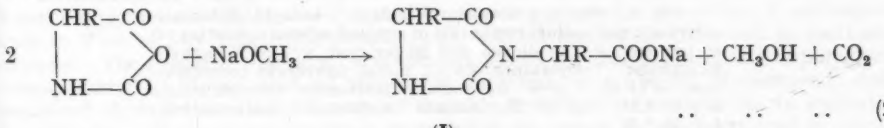
It is concluded that the main reactions are not those given by Berger *et al.* and that the titrations are essentially a determination of the carbon dioxide produced by polymerisation of the anhydrides. The method is therefore only of value if the carbon dioxide is retained in solution. The most favourable conditions for this are indicated.

Berger, Sela and Katchalski[1] have claimed that N-carboxy-α-amino-acid anhydrides can be titrated in non-aqueous solutions with sodium methoxide in methanol, the course of the reactions being described by the equation—



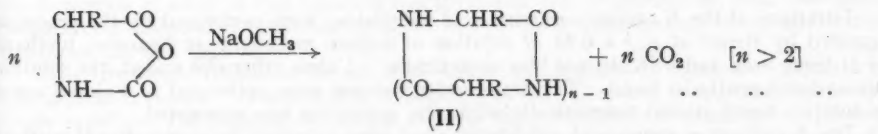
(1)

Recent studies in these laboratories[2] have shown that sodium methoxide is an extremely powerful catalyst for the polymerisation of several N-carboxy-α-amino-acid anhydrides, particularly those containing an unsubstituted >NH group. One molecule of sodium methoxide is capable of bringing about the rapid decomposition of many molecules of anhydride, so that the main course of the reaction is by no means confined to the processes represented by equation (1). On the other hand the following over-all reactions are of major importance (*vide infra*)—



(I)

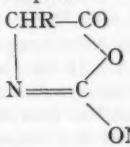
(2)



(II)

(3)

These equations do not represent the mechanism of the reactions. The initial process is believed to be the formation of the complex—



from the N-carboxy-α-amino-acid anhydride and sodium methoxide; this subsequently enters into reactions similar to those described by Ballard and Bamford,[4] which yield substituted hydantoin-3-acetic acids (**I**) and cyclic polypeptides (**II**). Open-chain polymers may also be produced. Sodium methoxide functions in these reactions essentially as a catalyst. The possibility of the formation of polymers and of hydantoin derivatives was not considered by Berger *et al.*,[1] and accordingly it becomes necessary to reassess the value of their titration technique as a method of determining N-carboxy-α-amino-acid anhydrides.

Experimental

The rates of evolution of carbon dioxide during the reaction of sodium methoxide with N-carboxy-γ-benzyl-L-glutamate anhydride in a mixed solvent (20 per cent. of N-methylformamide and 80 per cent. of dioxan by volume) at 25° C were followed in the constant-volume apparatus described previously by Ballard and Bamford.[3] The acid formed in tests with low sodium methoxide concentration was titrated potentiometrically in ethanol, antimony and calomel electrodes being used.

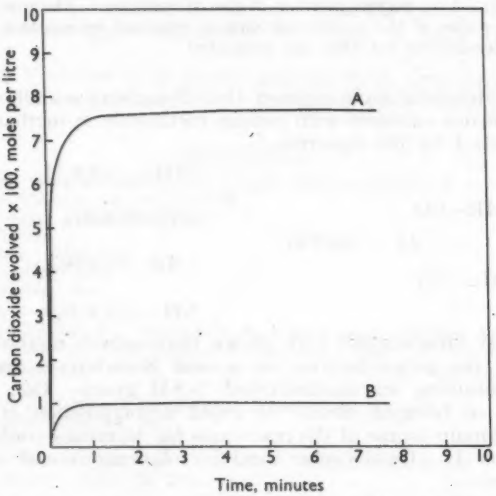


Fig. 1. Reaction between N-carboxy-γ-benzyl-L-glutamate anhydride and sodium methoxide in a mixed solvent consisting of 80 per cent. v/v of dioxan and 20 per cent. v/v of N-methylformamide. Temperature, 25° C; initial anhydride concentration, 0·11 *M*. Curve A, sodium methoxide concentration, 4×10^{-3} *M*; curve B, sodium methoxide concentration, 4×10^{-4} *M*

Titrations of the N-carboxy-α-amino-acid anhydrides were performed by the procedure suggested by Berger *et al.*,[1] a 0·45 *M* solution of sodium methoxide in benzene - methanol (1+1) being used and with thymol blue as indicator. Unless otherwise stated, the solutions were agitated gently by hand. Titrations under vacuum were performed in a closed vessel, the solution being stirred magnetically while the apparatus was evacuated.

The N-carboxy-α-amino-acid anhydrides used were prepared by conventional methods and were recrystallised until free from chloride.

Results and discussion

Some features of the reaction between N-carboxy-γ-benzyl-L-glutamate anhydride and sodium methoxide are indicated in Fig. 1. It has been established that the reaction is comparatively rapid, even at very low concentrations of sodium methoxide, and further, particularly under these conditions, more carbon dioxide is evolved than is equivalent to the sodium methoxide. It is clear that one of the major reactions occurring is polypeptide

formation. Significant quantities of acids (probably the corresponding substituted hydantoin-3-acetic acids) are formed, and can lead to a rapid termination of the reaction after a comparatively small conversion of the N-carboxy-α-amino-acid anhydride (see curve B, Fig. 1). With high concentrations of sodium methoxide, the final degree of conversion of the anhydride may approach 100 per cent., although some carbon dioxide remains in solution as sodium methyl carbonate (curve A, Fig. 1).

These results suggest strongly that the technique of Berger *et al.*[1] really determines the carbon dioxide liberated and does not necessarily depend on the occurrence of the reactions shown in equation (1). In these circumstances it is to be expected that the titre would depend on the extent to which the carbon dioxide is retained in solution, in particular on the nature of the solvent, the rate of addition of sodium methoxide and the rate of shaking. These expectations have been fully confirmed by experiment. It may be seen from the typical results given in Table I that the apparent equivalent increases (corresponding to

TABLE I

DEPENDENCE OF APPARENT EQUIVALENT WEIGHT OF DL-PHENYLALANINE-N-CARBOXY-α-AMINO-ACID ANHYDRIDE ON CONDITIONS OF TITRATION

Calculated equivalent weight 191

Solvent	Initial concentration of anhydride	Approximate duration of titration, minutes	Observed equivalent weight	Comments
Toluene ..	0·072	2·5	200	
		7·5	230	
		15	330	
Ethyl acetate	0·52	5	215	little shaking
		5	238	moderate shaking
		5	252	vigorous shaking
Toluene ..	0·026	3	374	nitrogen bubbled through liquid
		3	467	liquid under vacuum

increasing loss of carbon dioxide) as the rate of titration is decreased or the rate of shaking increased. Also, if deliberate attempts to remove carbon dioxide are made by bubbling nitrogen through the liquid during titration, or carrying out the determination under reduced pressure, very high values are obtained. Similar results have been obtained with other N-carboxy-α-amino-acid anhydrides in other solvents.

Evidence that only a minor part of the reaction follows equation (1) in the case of N-carboxyglycine anhydride was obtained by titrating a solution containing 2 milli-equivalents in 2 ml of NN-dimethylformamide with sodium methoxide dissolved in methanol-benzene. The apparent equivalent was 196 (calculated 101) and a precipitate of polyglycine corresponding to 65 per cent. of the initial anhydride was formed. Colorimetric determination[4] showed that 10·4 per cent. of the anhydride had been converted to hydantoin-3-acetic acid. It should be noted that, provided all the carbon dioxide is retained in solution, the formation of acids of this type will not invalidate the determination, since two moles of N-carboxy-α-amino-acid anhydride yield one mole of carbon dioxide and one of acid (compare equations (2) and (3)).

The titrimetric results of Berger *et al.* show only apparently random departures from the calculated values. This probably indicates that their titrations were performed comparatively rapidly. The isolation by Berger *et al.*[1] of the products corresponding to equation (1) is understandable if the reaction was carried out by rapid mixing of equivalents of the N-carboxy-α-amino-acid anhydride and sodium methoxide, as seems probable. These are not, of course, the conditions existing during titration

To summarise, the determination of N-carboxy-α-amino-acid anhydrides by titration with sodium methoxide in non-aqueous solution can yield erroneous results unless care is taken to work under conditions such that no carbon dioxide is lost from the liquid. The favourable conditions are a low concentration of anhydride (preferably less than 0·05 *M*), a medium in which carbon dioxide is very soluble, rapid addition of alkali and a minimum of shaking. A suitable practical procedure is to dissolve 0·2 to 0·5 millimoles of the anhydride in 10 ml of dry solvent, *e.g.*, ethyl acetate, chloroform, acetone or ether, and titrate with a

standard solution (0·1 *M*) of sodium methoxide in a mixture of equal volumes of methanol and benzene. A solution of thymol blue in methanol is satisfactory as indicator. The alkali should be added rapidly so as to complete the titration within 1 minute. Vigorous shaking should be avoided, and the liquid should preferably be cooled. Alternatively, excess of sodium methoxide may be added to the N-carboxy-α-amino-acid anhydride and the excess determined by titration with, for example, a solution of benzoic acid in methanol. Thymol blue is again a suitable indicator.

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October 20th, 1955

An Automatic Fischer Titration Unit for Laboratory Use

BY J. F. BROWN AND W. F. VOLUME

The determination of the moisture content of many compounds, especially organic liquids, is normally carried out by titration with the Karl Fischer reagent, which is a solution of iodine, sulphur dioxide and pyridine in methanol. The end-point of the reaction can be detected electrically by electrode polarisation, the so called dead-stop end-point. The voltage change across the electrodes at the end-point has been studied, and a circuit has been designed in which use is made of this voltage change to control automatically the addition of the Fischer reagent during a titration, the flow of the reagent from the burette being through a solenoid-operated valve. Owing to a time lag of several seconds between addition of reagent and the completion of the reaction, a timing device is incorporated in the circuit to permit temporary end-points to be distinguished from the final true end-point. An automatic titration unit incorporating these features has been built. It can be used for automatic direct or back-titrations and can also be used for normal manual titrations. The unit has been installed for routine use, and the results have shown that, by eliminating personal factors, it gives increased accuracy and reproducibility.

THE determination of the moisture content of many compounds, both organic and inorganic, may be conveniently carried out by use of the Karl Fischer reagent. This reagent consists of pyridine, iodine and sulphur dioxide in a methanol solution, and reacts with water so that the free iodine is removed, being converted to hydriodic acid. Hence the Fischer reaction can be used to titrate materials containing water, the end-point being indicated by the presence of free iodine. A feature of the Fischer reaction, however, is that there is a time lag of some seconds between the addition of the reagent and the completion of the reaction. Therefore, as the end-point is approached premature end-points are indicated, excess of iodine being present momentarily. The normal procedure in manual titrations is to add Fischer reagent until excess of iodine persists in the solution for about 15 to 20 seconds, the excess of iodine being detected visually or electrically by the polarisation dead-stop effect. Longer times are not advisable, since the liquid may pick up water from the air, or side-reactions with the iodine may occur. However, by adherence to a uniform technique, reproducible results can be obtained by the direct titration.

Many workers have favoured a back-titration method, in which excess of Fischer reagent is added and the unused reagent is titrated with a standard water - methanol solution.

Since this involves a double standardisation and a double titration with little increase in accuracy, the direct method is normally used for routine work in I.C.I. Billingham laboratories.

The advantages of an automatic direct-titration unit with dead-stop end-point for routine laboratory use are many. It eliminates all personal errors and gives better reproducibility and accuracy; it permits titrations to be carried out with the minimum of attention on the part of the operator and can be used by operators unfamiliar with the Fischer technique. It can be used with coloured samples and, when large numbers of routine samples are analysed, time and labour can be saved, mainly because no supervision of the apparatus during titration is needed.

Characteristics of dead-stop end-point

The dead-stop end-point is based on the fact that the Fischer reagent acts as a depolariser towards a pair of platinum electrodes immersed in the reactants. If a small current is passed through the cell, these electrodes are polarised as long as excess of water is present and hence a back e.m.f. is developed. However, on the addition of excess of Fischer reagent the electrodes are depolarised and the back e.m.f. drops to zero. Thus the end-point can easily be detected by measuring the voltage drop across the cell when a constant current is passed.

Measurements of the current - voltage characteristics of a cell with platinum electrodes were made at different stages of the titration. The results showed that with excess of water a back e.m.f. due to polarisation of about 500 mV was built up for currents of between 10 and 100 μA (see Fig. 1).

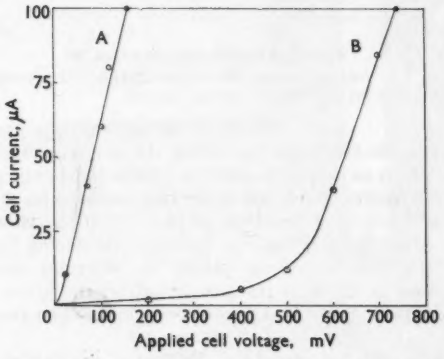

Fig. 1. Current - voltage characteristics of cell with platinum electrodes: curve A, with excess of Fischer reagent; curve B, with excess of water

The operating current chosen, 100 μA, was selected because it gave a rapid build up of the polarisation voltage without causing any noticeable electrolysis of the solution. The applied voltage across the cell, with a constant current of 100 μA, during a typical titration is shown in Fig. 2. This was obtained by direct measurement, 15 seconds being allowed after each addition of reagent for the reaction to take place. The steepest part of the curve is at about 300 mV and this is therefore taken as the end-point.

Experimental

The apparatus is illustrated in Figs. 3, 4 and 5. Although it is not an entirely automatic unit, it is automatic so far as the titration itself is concerned. The reagent starts to run from the burette when a switch is pressed and stops when the correct end-point is reached. Different coloured lights indicate the running period, the false end-points and the correct end-point, one light being on for each state.

Part of the apparatus is mounted on a stand, with two burettes, reagent reservoirs and the cover plug of the reaction vessel fixed. The reaction vessel is fitted to the plug from below and held in position by the stirrer unit.

The electronic unit supplies the current for the electrodes, measures the voltage across them and controls the flow of reagent from the burette by means of the solenoid valve.

It has a number of switches and controls for adjusting the delay before an end-point is accepted as correct, for changing over from normal to reverse titration and so on. The titration can also be stopped at any time for refilling the burette, or can be carried out by hand. Operation for a direct titration proceeds as follows.

The titration vessel and the burette are filled, and the electronic unit is switched on with the TITRATION DIRECTION switch in the forward position. When the START switch is pressed, the solenoid valve opens, reagent being delivered into the flask, and the green light comes on.

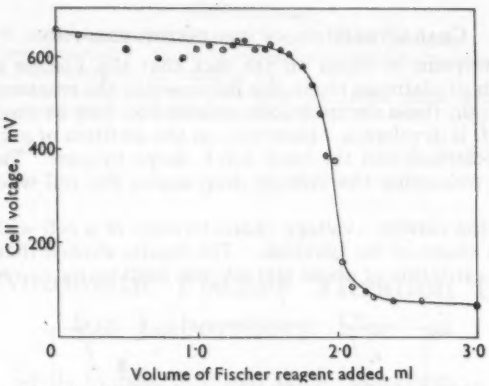

Fig. 2. Voltage across electrodes during a titration, a constant current of 100 μA being passed

When the voltage across the electrodes drops below the set triggering voltage, the solenoid valve closes, the timing circuit is switched on and the yellow light comes on. Two possibilities now arise. If the voltage remains below the triggering voltage for more than the set time, *i.e.*, the permanent end-point has been reached, at the end of the time interval the red light comes on and no further titration takes place. However, if during the set time interval the electrode voltage rises above the triggering value, the solenoid valve again opens, more reagent being added, the time interval is reset to zero and the green light comes on again. The cycle is repeated until a permanent end-point is reached, when the flow is finally stopped and the red light comes on.

Operation for a back-titration is similar. With the TITRATION DIRECTION switch in the forward position, excess of Fischer reagent is added by operating the MANUAL switch, which actuates the solenoid valve on the Fischer burette. The TITRATION DIRECTION switch is moved to the position for back-titrations, and the START switch pressed. This opens the solenoid valve on the second burette, which adds standard water - methanol reagent until the end-point is reached, when the unit will switch itself off as before.

BURETTE ASSEMBLY—

This comprises a 10-ml Pyrex-glass burette fitted with a B7 cone joint in place of the normal tap. The burette is fixed into the solenoid-operated valve by means of wax. The reservoir containing the Fischer reagent is a Winchester bottle, and the reagent can be pumped up into the burette by means of a small hand aspirator. When the pressure in the flask is released, the excess of reagent syphons back into the reservoir, thus filling the burette to a constant level. A calcium chloride drying tube prevents moisture reaching the Fischer reagent. Another identical assembly containing standard water - methanol solution is provided.

SOLENOID VALVE—

The flow of reagent from the burette into the titration vessel is controlled by a solenoid-operated glass valve (see Fig. 6). This valve employs a glass plunger that is ground to fit over a convex seat to give a leak proof seal. The glass plunger has a soft iron core. The

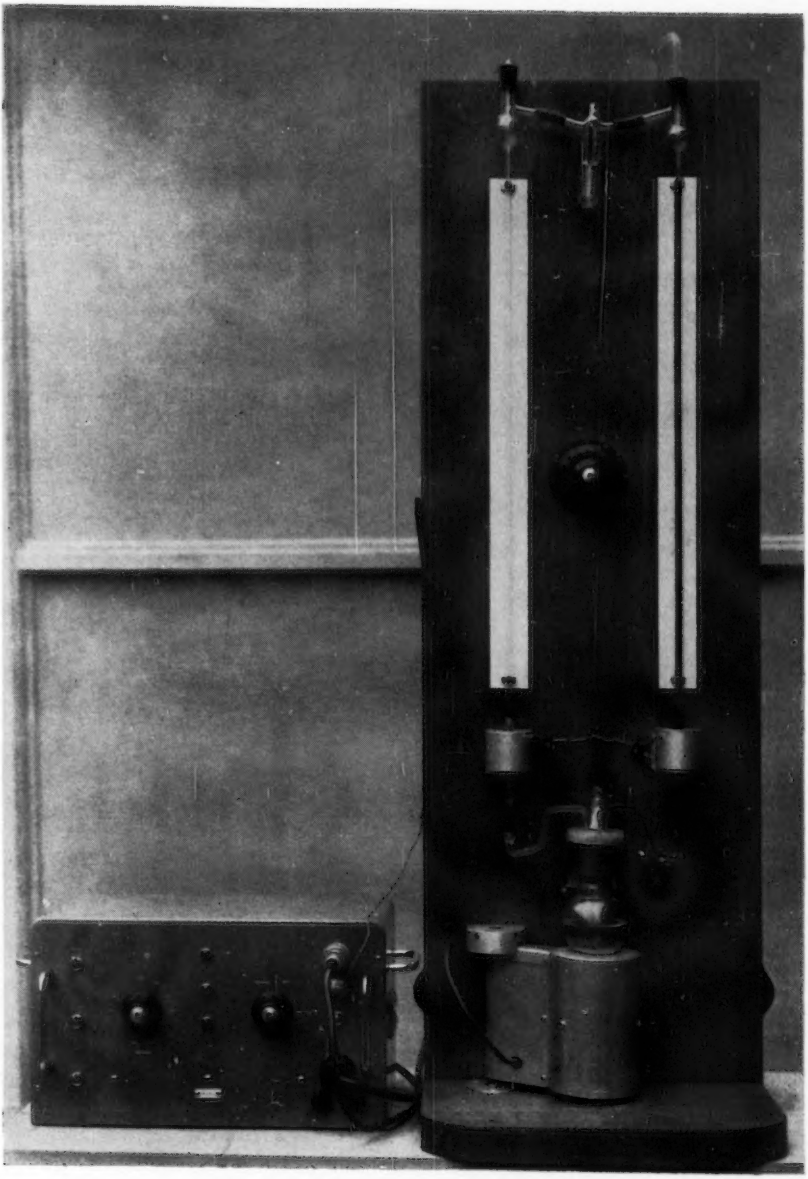

Fig. 3. View of complete titrator, comprising titration stand and electronic control unit

[To face p. 310

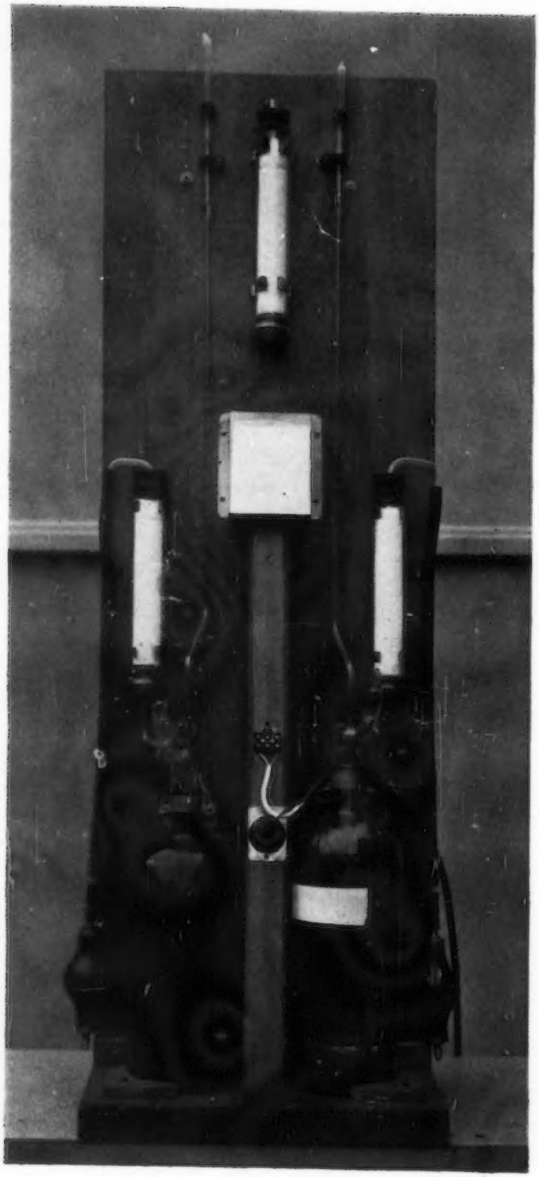

Fig. 4. Rear view of titration stand

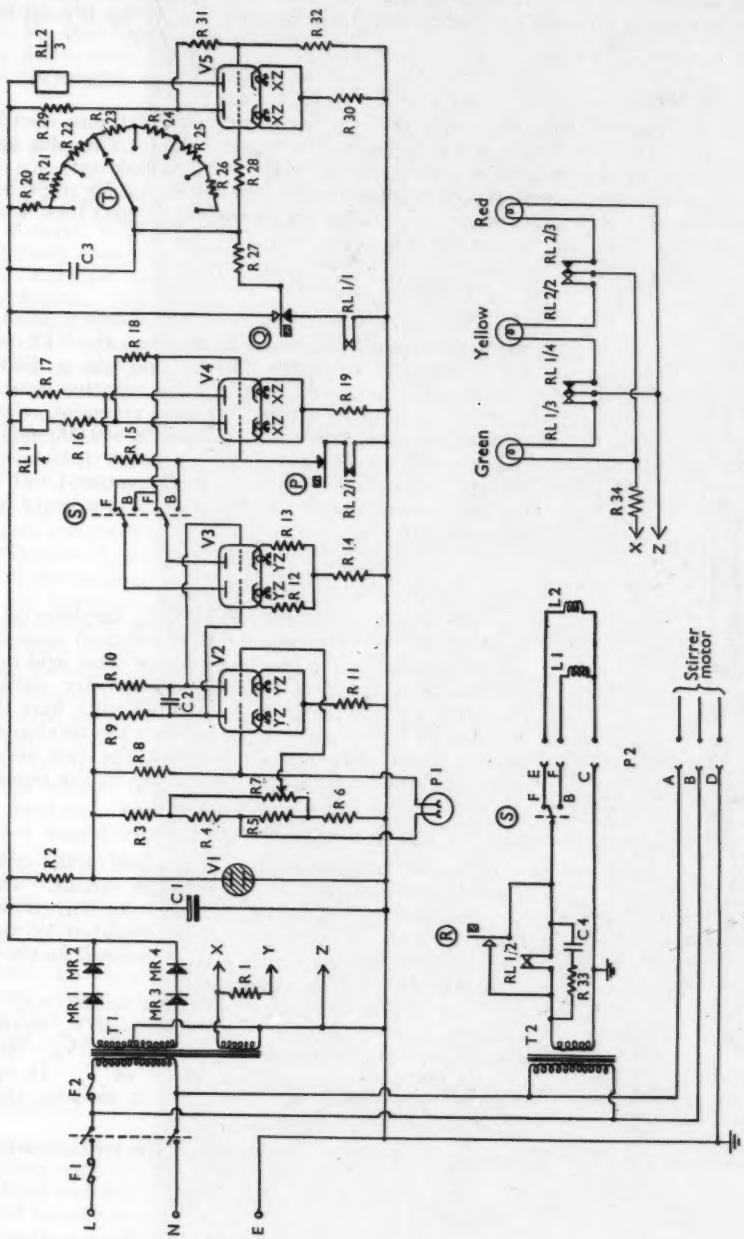

Fig. 5. Circuit for electronic control unit (for values of components, see Appendix, p. 315)

valve is surrounded by an iron-shrouded coil of 5000 turns of 36 s.w.g. copper wire, which when energised (50 volts a.c.) raises the plunger, so permitting liquid to flow out. The valve terminates in another B7 cone joint on to which the burette delivery tip is fixed by means of wax.

TITRATION VESSEL—

The burette delivery tip, the sample filling tube and the two platinum electrodes are mounted in a polythene plug, which is attached to the burette stand. This plug has a B34 taper and is a tight fit into the neck of a standard 150-ml flask. This flask rests on a magnetic stirrer motor, which can be moved aside to allow the flask to be lowered for emptying. The electrodes each consist of 0·5-mm diameter platinum wire sealed into a glass tube, with ½ inch of wire outside the tube in a loop as the actual electrode.

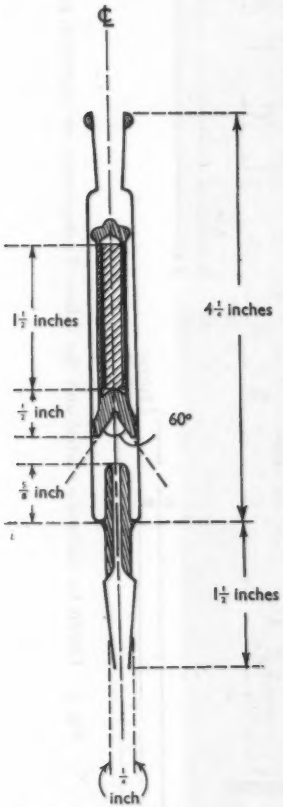

Fig. 6. Solenoid-operated glass valve

CELL CURRENT SUPPLY—

The current to the electrodes is obtained from resistor chains (see circuit diagram, Fig. 5) across the NT2 neon tube, V_1. Connection is made to the cell via a Belling Lee "Screenector" plug and socket. The negative terminal A is at about +3 volts relative to ground potential, whereas the positive terminal B is taken through a 680,000-ohm resistor to the +60-volt supply from the neon tube. Since the voltage across the cell is always small compared with 60 volts, the cell current is constant (to about 1 per cent.) at rather less than 100 μA.

VOLTAGE-AMPLIFYING STAGE—

The double triode, type ECC81, V_2, amplifies by a factor of about 20. It is connected as a balanced stage with the cell voltage applied to one grid and the other grid taken to a zero-set potentiometer. This potentiometer permits the triggering level to be set at the desired value over the range of differences in characteristics between the two halves of the valve. A 0·1-μF condenser between the two anodes cuts down any hum voltage due to pick-up in the input circuit.

TRIGGER CIRCUIT—

The anode voltages of V_2 are taken to the grids of V_3, the first valve of the two-valve trigger circuit. The circuit is of the Eccles - Jordan type, in which the normal resistances from the grids of V_4 to ground are replaced by the anode resistances of the two halves of V_3, increased by the addition of 22,000-ohm cathode resistors.

This arrangement gives a trigger action with a stable backlash of about 1·5 volts at the grids of V_3, equivalent to about 75 mV at the input, *i.e.*, the grids of V_2. Relay RL1 is a 20,000-ohm relay in one anode of V_4. It opens the solenoid valve when energised, and it initiates the timing circuit when de-energised.

The coupling from V_3 to V_4 is made via a change-over switch, S, the TITRATION DIRECTION switch.

TIME-DELAY CIRCUIT—

The fourth double triode, V_5, is in the time-delay circuit. In th erest state V_{5a} grid is connected via the switched resistor T to the high-tension line and V_{5a} is therefore conducting while V_{5b} is cut off by the inter-valve Schmitt coupling. When a titration is started, the 4-μF condenser connected to the grid of V_{5a} is charged to ground potential and is maintained

there until the end-point is reached. Then the 4-μF condenser discharges exponentially towards the high-tension line and if the end-point indication is maintained for the selected time interval, the voltage on the grid of V_{5a} rises to its triggering level, which is about 100 volts; V_{5a} then conducts while V_{5b} is cut off and RL2 is de-energised.

Time delays of 5, 10, 15, 20, 30, 45 and 60 seconds are set by switching in different values of discharging resistance with switch T.

RELAYS AND SWITCHES—

Two relays, RL1 and RL2, are used in the anode circuits of V_4 and V_5, respectively. Both are of the Post Office Type 3000 and have 20,000-ohm coils. The energising current for each is under 3 mA and in the circuit they pass about 4 mA.

A normally open contact of RL1 is used to switch power to the solenoid. A series combination of a 0·1-μF condenser and a 100-ohm resistor is connected across the contacts for spark suppression. During titration, both relays are energised; RL2 alone is energised during the delay period after a preliminary end-point is reached, whilst both are de-energised at the end of the delay period and when the instrument is in the rest state. This is achieved by using one normally open contact of RL1 to initiate the time delay, and by using one normally closed contact of RL2 in series with a normally closed biased switch P from the grid of V_{4a} to ground. Until this biased switch is opened RL1, and hence also RL2, is maintained unenergised. When P is opened, if the voltage input is on the correct side of the triggering value, RL1 is energised and the grid of V_{5a} is connected to ground, thereby energising RL2. When a preliminary end-point is reached, RL1 is de-energised and the voltage on the grid of V_{5a} gradually rises. Should the input return to the original side of the end-point, RL1 is again energised and the grid of V_{5a} is returned to ground potential. When a stable end-point is reached, and RL1 remains de-energised for the selected time interval, V_{5a} conducts and RL2 is de-energised. Both RL1 and RL2 stay de-energised until P is opened and the sample is on the original side of the end-point.

A second biased switch, Q, is used to permit the titration to be stopped at any moment. The 10,000-ohm resistor through which the 4-μF condenser is charged to ground potential is also used for rapid discharging of the condenser when switch Q is operated. This results in the de-energising first of RL2 and then of RL1. The unit then remains in the rest condition until switch P is operated.

The Yaxley switch, S, is incorporated so that back-titration can be carried out if necessary. This switch interchanges the connections between valves V_3 and V_4, and has one pole that switches the solenoid supply to a second solenoid valve, which can control the addition of standard methanol - water reagent.

Another biased switch, R, is connected in parallel with the switch in the lead from the 50-volt supply to the solenoid. This permits Fischer reagent to be added manually with the switch S in the forward-titration position and water - methanol solution in the back-titration position.

Three indicator lights show the state of the relays. The bulbs used are rated at 6·3 volts and 0·3 amps, but are used at a reduced voltage to improve their life. Only one bulb is lit at a time. During a titration, when both RL2 and RL1 are energised, the green light is switched on. When a preliminary end-point has been reached and only RL2 is energised, the yellow light is on. Finally, at the end of the titration when both relays are de-energised, the red light is switched on. This is indicative of the rest condition of the unit.

POWER SUPPLY—

Two transformers are used, one with a 250–0–250 volt high-tension winding and a 6·3-volt heater winding supplies the electronic section, while a 50-volt transformer gives the solenoid power. Metal rectifiers with one smoothing condenser are used on the high-tension supply. This limited smoothing is adequate, since the current consumption is low and since a neon tube is used to stabilise the high-tension voltage to the first amplifying stage. The 6·3-volt heater supply is used directly for the heaters of V_4 and V_5, but is reduced by a series resistor to 5·5 volts before connection to the heaters of V_2 and V_3. A series resistor is also used in the lead to the indicating lamps to reduce the voltage.

OPERATION—

The unit has proved simple to operate and yields consistent reproducible results. The mode of operation for a normal titration is as follows—

1. Switch on unit.
2. To a clean dry flask add 25 ml of suitable solvent, *e.g.*, pyridine or methanol.
3. Fill the burette and place the flask in position.
4. Switch on the stirrer and adjust the control to give a suitable stirring speed.
5. Switch TIME-DELAY SELECTOR to the chosen time interval—15 seconds is suitable for most titrations.
6. Switch the TITRATION DIRECTION to forward.
7. Press START switch down and release.
8. When the red light comes on, indicating the end of the titration, the flask contains water-free solvent. Add a measured volume of sample to flask. This should be chosen to give a titration requiring not more than 10 ml of Fischer reagent.
9. Fill burette.
10. Press START switch down and release.
11. When red light comes on, read the burette.

If at any stage it is desired to stop the titration, the CUT-OUT switch may be pressed down and released. This will stop addition of Fischer reagent and the red light will come on. The titration may be restarted by pressing the START switch in the normal way.

For back-titrations the mode of operation is as follows—

1. Proceed with the preliminary operations as in the normal procedure to give water-free solvent in flask.
2. Add the sample.
3. With the TITRATION DIRECTION switch in the forward position, operate the MANUAL switch to add a known volume of Fischer reagent to give excess.
4. Fill the burette containing the water - methanol mixture.
5. Switch the TITRATION DIRECTION to the back position.
6. Press the START switch down and release.
7. When the red light comes on, read the burette.

RESULTS

The apparatus has been installed in the routine analytical laboratory and is being used to determine the water content of organic liquids, *e.g.*, acetone, *iso*propanol and methanol, some fifty samples per day being analysed. The apparatus gives results that are reproducible to better than $\pm$ 0·1 ml. This is as accurate as a good manual titration (see Tables I and II). In addition, the apparatus is simple to operate and can be used by operators unfamiliar with Fischer titrations.

Whereas the average time taken for a titration, about 5½ minutes, is slightly longer than that required for a manual titration, there is a saving in that for a substantial part of this time no supervision of the apparatus is required.

TABLE I

REPRODUCIBILITY TEST

10 titrations with 5-ml samples of refined methanol

3·50 ml of Fischer reagent ≡ 0·32 per cent. w/w of water

Sample No.	Titre, ml
1	3·48
2	3·50
3	3·54
4	3·40
5	3·36
6	3·40
7	3·50
8	3·40
9	3·45
10	3·43
Mean	3·45
Standard deviation	0·06

TABLE II

COMPARISON OF RESULTS BY AUTO TITRATOR AND BY MANUAL OPERATOR FOR METHANOL WITH VARIOUS WATER CONTENTS

Sample No.	Water found with auto titrator, % w/w	Water found with manual titrator, % w/w
1	0·07	0·08
2	0·11	0·13
3	0·17	0·17
4	0·20	0·22
5	0·25	0·25
6	0·35	0·34
7	0·44	0·43
8	0·47	0·46
9	0·56	0·56
10	0·41	0·42

APPENDIX

LIST OF COMPONENTS USED IN THE CONSTRUCTION OF THE CONTROL UNIT (Fig. 6)

R_1 = 1·5-ohm, wire-wound resistance.
R_2, R_9, R_{10} = 270,000-ohm, ½-watt, resistance.
R_3 = 180,000-ohm, ½-watt, resistance.
R_4 = 2200-ohm, ½-watt, resistance.
R_5 = 820-ohm, ½-watt, resistance.
R_6 = 8200-ohm, ½-watt, resistance.
R_7 = 100,000-ohm potentiometer.
R_8 = 680,000-ohm, ½-watt, resistance.
R_{11} = 47,000-ohm, ½-watt, resistance.
R_{12}, R_{13} = 22,000-ohm, ½-watt, resistance.
R_{14}, R_{28} = 470,000-ohm, ½-watt, resistance.
R_{15}, R_{18} = 2·7-megohm, ½-watt, resistance.
R_{16} = 6800-ohm, 1-watt, resistance.
R_{17}, R_{30} = 27,000-ohm, 1-watt, resistance.
R_{19} = 22,000-ohm, 1-watt, resistance.
R_{20}, R_{21}, R_{22}, R_{23} = 3·3-megohm, ½-watt, resistance.
R_{24} = 6·8-megohm, ½-watt, resistance.
R_{25}, R_{26} = 10-megohm, ½-watt, resistance.
R_{27} = 10,000-ohm, ½-watt, resistance.
R_{29} = 33,000-ohm, 1-watt, resistance.
R_{31} = 2·2-megohm, ½-watt, resistance.
R_{32} = 1-megohm, ½-watt, resistance.
R_{33} = 100-ohm, ½-watt, resistance.
R_{34} = 4·5-ohm wire-wound resistance.
C_1 = 32-μF electrolytic condenser.
C_2, C_4 = 0·1-μF condenser.
C_3 = 4-μF condenser.
V_1 = NT 2 stabiliser valve.
V_2, V_3, V_4, V_5 = ECC 81 valve.
P_1 = Input socket (Belling Lee "Screenector" type).
P_2 = 6-way socket (Plessey), power to solenoids and stirrer motor.
T_1 = Mains transformer: primary winding, 230 volts; secondary windings, 250–0–250 volts and 6·3 volts.
T_2 = Mains transformer: primary winding, 230 volts; secondary winding, 50 volts.
P = Biased-on switch (START).
Q = Biased change-over switch (CUT-OUT).
R = Biased-off switch (MANUAL).
S = Three-pole two-way rotary switch (Yaxley) (TITRATION DIRECTION).
T = Seven-way rotary switch (Yaxley) (TIME-DELAY SELECTOR).
F_1 = 2½-amp. fuse.
F_2 = 1-amp. fuse.
MR1, MR2, MR3, MR4 = RMO metal rectifiers.
L_1 = Water solenoid valve.
L_2 = Fischer solenoid valve.
RL1 = 20,000-ohm relay (2 makes and 1 change-over).
RL2 = 20,000-ohm relay (1 break and 1 change-over).

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Notes

RAPID KJELDAHL NITROGEN DIGESTION OF COFFEE-LEAF MATERIAL BY THE PERMANGANATE METHOD

As a part of the programme for investigations into soil nitrogen and the nitrogen nutrition of the coffee tree, we have recently undertaken the analysis of numerous coffee-leaf samples collected from experimental sites. In view of staff limitations resulting from the present conditions of unrest, a preliminary survey of recent literature describing methods, catalysts and catalytic mixtures was first made to see which of the several semi-micro techniques available would combine the greatest degree of accuracy, reproducibility and rapidity, while at the same time lending itself to satisfactory manipulation by a trained African laboratory assistant. Apart from techniques involving the use of mercury and selenium catalysts by Perrin,[1] Bradstreet[2] and McDonnell and Murphy,[3] the recent publications by Beet[4,5] describing the use of potassium permanganate were of interest. The use of this reagent for the digestion of coffee-leaf material was considered and some preliminary tests were made.

These very few early tests showed that the permanganate digestion technique was both practical and rapid, and a formally designed laboratory test was carried out in which it was compared with semi-micro digestion techniques with mercury oxide - potassium sulphate as the catalyst mixture[6] and selenium as the catalyst.[3] In addition to a direct comparison of the three digestion techniques, each was examined with and without the addition of *o*-thiolbenzoic acid, as suggested by McCutchan and Roth,[7] in order that traces of nitrate nitrogen would be included in one set of results by each digestion procedure, as well as to give a check on the use of this reagent with the permanganate method.

Experimental design and procedure

The design of the experiment was a balanced orthogonal 3×2 factorial, with four replications of each treatment, which required a total of twenty-four individual determinations. Analyses were carried out in batches of four on an electrically heated digestion stand with individual unit thermostatic control. All the digestions were performed at random, *i.e.*, they were not carried out in batches of four replicates at any one time. Sub-samples of air-dried leaf material were drawn from a single bulk sample prepared by grinding in a micro Wiley laboratory mill to pass a 40 U.S.A. standard-mesh sieve. The analyses were performed on 50-mg sub-samples, which were weighed folded in nitrogen-free cigarette papers. Digestions were carried out in 50-ml Kjeldahl flasks and the ammonia distillations were performed in a Scandrett apparatus,[8] modified in that the air condenser was replaced by a Liebig condenser, into 1 per cent. boric acid as described by Yuen and Pollard.[9] In this latter respect it was found that the use of either sodium thiosulphate or sodium sulphide to decompose mercurammonium compounds during distillation resulted in the acidification of the boric acid - mixed-indicator solution immediately before the ammonia distilled over, and this made the colour change of the titration end-point difficult to standardise. Blank determinations for reagents were performed with all the six differing combinations of digestion mixtures. All digestion mixtures contained 4 ml of concentrated sulphuric acid (plus a further 2 ml with the selenium catalyst) and 0·1 g of thiolbenzoic acid, when this was included.

Results

Table I summarises the mean results, the standard deviations for mean and for single analyses and the calculated average difference that would most probably occur between duplicate determinations on a sample by any one method. The last is included because duplicate determinations are standard practice for routine analytical work in the laboratory. Before considering the results in Table I, it is worth noting that the mean digestion-mixture values over determinations with and without *o*-thiolbenzoic acid, *i.e.*, mean of eight individual determinations, were not significantly different, neither were the interaction effects between *o*-thiolbenzoic acid and the three digestion methods. Differences between the mean values for digestion methods, *i.e.*, comparisons between 1*a*, 2*a* and 3*a* or 1*b*, 2*b* and 3*b* were not significant, but in all cases the difference between means for a given digestion method with and without *o*-thiolbenzoic acid, *i.e.*, comparisons between 1*a* and 1*b*, 2*a* and 2*b*, and 3*a* and 3*b*, were significant. The over-all mean difference between the three digestion methods with and without the addition of *o*-thiolbenzoic acid was very highly significant, showing the presence of nitrate nitrogen in the coffee-leaf sample. From a consideration of the standard deviations for both means of four determinations and for individual analyses

figures, the sulphuric acid - selenium - *o*-thiolbenzoic acid mixture has shown outstandingly consistent results. Methods 1*a*, 1*b* and 2*a* have given rather high values, whereas results by methods 3*a* and 3*b* are considered reasonable.

Discussion of results

For the purpose of the proposed investigations into Kjeldahl nitrogen values of coffee-leaf samples the maximum difference between duplicate determinations was required to be of the order of 10 to 12 milli-equivalents per 100 g of dry tissue. In terms of the approximate analytical values that would be obtained, this is 2·6 to 3·0 per cent. of the mean. Apart from the sulphuric acid - selenium - *o*-thiolbenzoic acid digestion mixture, the values in Table I for average differences between duplicate determinations are only satisfactory for the permanganate digestion methods.

Table I

Mean kjeldahl nitrogen values and standard deviations

	Sulphuric acid - mercuric oxide - potassium sulphate		Sulphuric acid - selenium		Sulphuric acid - potassium permanganate	
Digestion mixture	no *o*-thiol-benzoic acid (1*a*)	*o*-thiol-benzoic acid added (1*b*)	no *o*-thiol-benzoic acid (2*a*)	*o*-thiol-benzoic acid added (2*b*)	no *o*-thiol-benzoic acid (3*a*)	*o*-thiol-benzoic acid added (3*b*)
Means of 4 (milli-equivalents per 100 of dry tissue*)	386·0	406·0	389·0	410·2	389·6	406·9
Least significant difference (5% point) ..	13·4					
σ (means of 4 analyses)	4·7	6·1	7·4	0·28	2·6	2·7
σ (individual analysis) ..	9·5	12·1	14·8	0·57	5·2	5·3
Above as percentage	(2·5)	(3·0)	(3·8)	(0·14)	(1·3)	(1·4)
Calculated average difference between duplicate analyses, % ..	3·8	3·4	4·3	0·16	1·5	1·6

	Digestion mixtures with *o*-thiolbenzoic acid	Digestion mixtures without *o*-thiolbenzoic acid
Means of 12 (milli-equivalents per 100 g of dry tissue)	407·7	388·5
Least significant difference	5% point = 7·8; 0·1% point = 14·8	
General experiment mean	398·1 ± 8·9	
Coefficient of variation, %	2·2	

* A nitrogen valency of 3 is assumed.

Further, the times required to complete digestions, batches of four at a time, were 4 hours by methods 1*a* and 1*b*, 1 hour and 20 minutes to 1 hour and 40 minutes for methods 2*a* and 2*b*, and 15 to 20 minutes for methods 3*a* and 3*b*; addition of concentrated sodium hydroxide immediately before distillation proved to be safer for the permanganate digest, whereas undue haste in the addition of this reagent to the other types of digest frequently resulted in accidents and the loss of a determination. It was decided therefore to employ the permanganate method for the routine Kjeldahl nitrogen determination with the addition of *o*-thiolbenzoic acid.

Subsequently, statistical analysis of sets of coffee-leaf results have confirmed the original choice of digestion method. The standard deviation of a single determination is 5·0 milli-equivalents per 100 g of dry tissue (1·2 per cent.) or less, and the standard error of the mean of duplicate determinations is of the order of 3·5 milli-equivalents per 100 g of dry tissue (0·9 per cent.). This degree of accuracy and reproducibility coupled with the rapidity of the digestion and distillation procedures has proved satisfactory for the purpose of the investigation and the method is suitable for routine analyses by a trained African laboratory assistant.

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THE RAPID DETERMINATION OF TRACES OF NICKEL IN COPPER SALTS

This method is based on work by Johnson and Simmons,[1] who described the use of nioxime as a colorimetric reagent for nickel. In the absence of a stabiliser the pink nickel - nioxime complex formed in aqueous ammoniacal solution is gradually deposited on standing, but if the solution is shaken with benzene the complex collects in the interface between the two layers. Copper forms a khaki coloured complex, which is not removed from the aqueous layer in this way. Provided that enough nioxime is added to deal with all the copper and all the nickel, the nickel complex can be separated from the copper. A double extraction into benzene is recommended. If only one extraction is used, traces of copper are carried through the procedure and impart a slight yellowish hue to the pink solution obtained for the final comparison with standards.

Method

Take 10 ml of solution containing 0·1 g of copper sulphate (≡ 0·025 g of copper) in a separating funnel and add 1 ml of 5 *N* ammonia solution. This is sufficient to form the cuprammonium complex. Add 40 ml of water and 20 ml of a 0·85 per cent. aqueous solution of nioxime. Mix and shake vigorously with 15 ml of benzene. Allow to separate (this takes between 30 and 45 minutes), and run off and discard all but 1 ml of the aqueous layer. Wash the organic layer with three 25-ml portions of *N* ammonia solution and finally with 25 ml of water. In each case 1 ml of the aqueous layer is retained when the washing liquor is run off and discarded. Extract the nickel from the interface with 5 ml of *N* hydrochloric acid. Separate the aqueous layer into another separating funnel, and wash the benzene with 5 ml of water, adding the washings to the separated nickel solution. To the 10 ml of aqueous solution add 6 ml of *N* ammonia solution and 0·5 ml of nioxime solution. The liquid should now be ammoniacal. Shake vigorously with 10 ml of benzene. Repeat the washing process and the extraction of nickel back into the aqueous phase with *N* hydrochloric acid as described above. Make ammoniacal with 6 ml of *N* ammonia solution and add 0·5 ml of nioxime solution. Compare the colour produced with standards prepared by adding 1 ml of *N* ammonia solution and 0·5 ml of nioxime solution to 15 ml of solution containing aliquots of standard nickel solution (1 ml = 0·01 ml of nickel). For large amounts of nickel it may be necessary to stabilise the colour by the addition of gum arabic solution.

Results

By this method 0·005 mg of nickel can be detected. This is equivalent to 0·02 per cent. in copper metal. Quantities of nickel between 0·005 and 0·03 mg were each added to 0·1 g of copper sulphate dissolved in 10 ml of water. The nickel was extracted by the method described above and assessed by visual comparison with standards covering the range 0·005 to 0·03 mg. In all tests a full recovery was obtained.

The authors are indebted to the Directors of Hopkin and Williams Ltd. for permission to publish this Note.

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October 25th, 1955

British Standards Institution

NEW SPECIFICATIONS*

B.S. 2710 : 1956. Bromomethane (Methyl Bromide). Price 2s. 6d.
B.S. 2711 : 1956. *cyclo*Hexanone. Price 2s. 6d.
B.S. 2712 : 1956. Dipentene. Price 2s. 6d.

Book Reviews

OFFICIAL METHODS OF ANALYIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Edited by WILLIAM HORWITZ. Eighth Edition. Pp. xvi + 1008. Washington, D.C.: The Association of Official Agricultural Chemists. 1955. Price $12.00 (in U.S.A.); $12.50 (elsewhere).

The eighth edition of the "Methods of Analysis" by the A.O.A.C. is marked by a tendency towards a methodological simplification, made possible by the use of chromatographic and instrumental technique; for example, the identification and determination of synthetic colours in food is now effected by means of chromatography and spectrophotometry.

A large-scale collaborative study, carried out in co-operation with the American Oil Chemists' Society on a variety of foods and fertilisers, has resulted in the adoption of a single catalyst, mercury, in Kjeldahl's method for the determination of nitrogen, and the abandonment of copper and selenium for any kind of material. This return to the use of a single catalyst will doubtless be welcomed by those chemists who have long believed that mercury gives the best results.

Amongst new subjects are a chapter on emission spectrometry and flame photometry for sodium and potassium in plants; methods for determining the stereochemical composition of amphetamines by polarimetry and mixed-melting-point comparison; a section on the optical crystallographic examination of crystalline substances and tables giving the optical crystallographic properties of antihistamines, barbiturates, sulphonamides and sympathomimetic amines and reineckates of quaternary ammonium compounds; a section on hormones includes absorptiometric methods for the determination of diethylstilbesterol and β-estradiol, formerly assayed biologically.

With the exception of mercury and parathion, the pressing need for methods for determining residual pesticides on plants of sufficient specificity and sensitivity to warrant inclusion has not yet been met.

When one considers the multiplicity of subjects covered and the number of tested and reliable methods contained in this book, it is not surprising that, despite sundry omissions and an extension of the system of abbreviation, its covers should now be farther apart than ever. F. L. OKELL

SYNTHETIC DRUGS. By H. RONALD FLECK, M.Sc., F.R.I.C., F.R.M.S. Pp. viii + 380. London: Cleaver-Hume Press Ltd. 1955. Price 70s.

The author tells us his ambition has been to write a book that would collate the synthesis, analysis and clinical uses of synthetic drugs. Furthermore, he hopes that students in the three allied professions of medicine, pharmacy and chemistry will find the work helpful. Yet other claims are that it will be welcomed by physicians and that it will certainly be a well thumbed tool on the desks and in the laboratories of all concerned with the production, study, testing and supply of synthetic drugs. An optimistic hope for 340 pages where "500 beautifully printed structural formulae clarify the chemical principles" but take up a good portion of the volume.

The groups of drugs are treated in 15 chapters based on their therapeutic use. With the multiplicity of names given commercially to each medicinal chemical marketed, any author would have considerable difficulty in deciding which one he would use as the title to a monograph. It would have been logical where there is a current official pharmacopoeial name or where an approved name has been adopted, to use it to head the monograph (chloramphenicol, phemitone, antazoline, diphenydramine, promethazine, isoprenaline, neostigmine, riboflavin and folic acid to name a few); in many instances the author has not done so, although in others he has used it. However, an excellent index does overcome this difficulty and the list of alternative names is useful.

Of the substances discussed there is information on synthesis, properties, analysis and testing and clinical data; as to be expected, most of the drugs are described in official publications. Structural formulae and methods of synthesis are set out clearly and this part of the book is the best.

* Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

Descriptions of analysis and testing are so cursory that they are valueless, and somehow it seems unlikely that a physician would turn to this volume for clinical information when he has "Martindale" at hand.

The publishers must be congratulated on the production of a most elegantly printed book and only a few mistakes were noticed: cyclizine is not a synonym for chlorcyclizine, and tryparsol and antazoline are mis-spelt. However, on consideration it is difficult to see to whom this book would be of much value in the practice of his profession; hence it would seem the author has been too ambitious in the scope selected.

D. C. GARRATT

Publications Received

THE CHEMICAL CONSTITUTION OF NATURAL FATS. By T. P. HILDITCH, C.B.E., D.Sc., F.R.I.C., F.R.S. Third Edition. Pp. xx + 664. London: Chapman & Hall Ltd. 1956. Price 95s.

METHODS OF BIOCHEMICAL ANALYSIS. Volume III. Edited by DAVID GLICK. Pp. x + 437. New York and London: Interscience Publishers Inc. 1956. Price $9.50; 75s.

CZECHOSLOVAK FINE CHEMICALS STANDARDS. Volume I. Prepared by a committee (Chairman: J. JELÍNEK, Sc.D.) of the Czechoslovak Standard Institution; edited by N. J. NEDELJAK. Pp. 544. Prague, Czechoslovakia: Chemapol. 1955. Free of charge on request from Chemapol, Panská 9, Praha 3, Czechoslovakia.

PHYSICAL ASPECTS OF ABSORPTIOMETRIC ANALYSIS. SPECIAL REPORT NO. 55. By the Methods of Analysis Committee, Metallurgy (General) Division, British Iron and Steel Research Association. Pp. vi + 37. London: The Iron and Steel Institute. 1956. Price 25s.

ESSENTIALS OF QUANTITATIVE ANALYSIS. AN INTRODUCTION TO THE BASIC UNIT OPERATIONS. By A. A. BENEDETTI-PICHLER. Pp. xiv + 666. New York: The Ronald Press Company. 1956. Price $15.00.

Erratum

MARCH (1956) ISSUE, p. 152, 11th line of "DISCUSSION." *For* "1 mg" *read* "1 μg."

REPORT OF THE ANALYTICAL METHODS COMMITTEE: VITAMIN B_{12}

THE Report prepared by the Vitamin-B_{12} Panel, "The Estimation of Vitamin B_{12}," reprinted from *The Analyst*, March, 1956, **81**, 132–136, is now available from the Secretary, The Society for Analytical Chemistry, 7–8 Idol Lane, London, E.C.3: price to members 1s. 6d., or to non-members 2s. 6d. Reports of the Analytical Methods Committee are only obtainable from the Secretary (not through Trade Agents) and remittances must accompany orders.

Papers for Publication in *The Analyst*

THE Editor welcomes Papers and Notes for insertion in *The Analyst*, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

A copy of the current Notice to Authors, last published in full in *The Analyst*, 1956, **81**, 127, can be obtained on application to the Editor, *The Analyst*, 7–8 Idol Lane, London, E.C.3. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment.

A few copies of the tabulated "Nomenclature of Vitamins," reprinted from *The Analyst*, 1953, **78**, 72, are also available.